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ELECTROCHEMICAL TREATMENT OF TANNERY EFFLUENTS

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DEDICATION

All the blood, sweat, tears, longings, desires, wishes, loneliness, emotions, success, smiles, joy, happiness..... everything put into this work is dedicated to

my wife Ester Cristina Nápoli Caliari, my eternal girlfriend, the fire that burns in my heart, my eternal flame, the invincible and tireless bravery, who with strength and dedication guided our family with wisdom and devotion in my absence

my daughter Dominique Nápoli Caliari, my warrior

my daughter Domitila Nápoli Caliari, my flower

my son Dante Nápoli Caliari, my prince

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To the profound mystery of the Quinta de Santo António .....

Não sou escravo de ninguém
Ninguém, senhor do meu domínio
Sei o que devo defender
E, por valor eu tenho
E temo o que agora se desfaz
Não me entrego sem lutar
Tenho ainda coração
Não aprendi a me render
Que caia o inimigo então

Metal Contra as Nuvens – Legião Urbana (1991)

Minhas raízes estão no ar
Minha casa é qualquer lugar
Se depender de mim
Eu vou até o fim
Cada célula
Todo fio de cabelo
Falando assim
Parece exagero
Mas se depender de mim
Eu vou até fim

Até o Fim - Engenheiros do Hawaii (2003)

Don't stop believin'

Don't Stop Believin' - Journey (1981)

"O tempo engana aqueles que pensam que sabem demais, que juram que pensam. Existem também aqueles que juram sem saber."

Sobre o tempo – Nenhum de Nós (1990)

RESUMO ALARGADO

Os efluentes das indústrias de couro são altamente complexos e contêm concentrações elevadas de produtos orgânicos, sais e outros produtos químicos tóxicos que inibem a atividade de micro-organismos durante as oxidações biológicas, nomeadamente, sulfuretos e crómio. Assim, os processos biológicos não são capazes de depurar totalmente as águas residuais provenientes desta indústria. Como alternativa à utilização dos processos biológicos para o tratamento de águas residuais com cargas poluentes elevadas tem sido estudada a aplicação de processos de oxidação eletroquímica no tratamento de resíduos aquosos.

Neste trabalho estudou-se a aplicação da oxidação eletroquímica no tratamento de amostras de efluentes provenientes da indústria dos curtumes, clarificadas ou não. Os ensaios de oxidação eletroquímica foram realizados sob condições galvanostáticas num reator eletroquímico equipado com ânodos de óxidos metálicos, $Ti/Pt/PbO_2$ e $Ti/Pt/SnO_2$-Sb_2O_4, e de diamante dopado com boro (BDD), utilizando diferentes densidades de corrente. A clarificação das amostras foi realizada por coagulação química (com iões de ferro ou alumínio) ou eletrocoagulação (com elétrodos de ferro ou alumínio). Para além disso, estudou-se a cinética da conversão do S^{2-} em SO_4^{2-}, com soluções aquosas de S^{2-} (60 mM), por eletro-oxidação, utilizando ânodos de BDD.

Para o estudo da cinética da conversão de S^{2-} em SO_4^{2-} foram realizados ensaios a diferentes densidades de corrente, que variaram entre 10 e 60 mA cm^{-2}. A duração dos ensaios variou com a densidade de corrente aplicada, tendo sido de 42 h para 10 mA cm^{-2} e de 10 h para 60 mA cm^{-2}. Os resultados mostraram que a conversão eletroquímica ocorre em etapas, através da produção de outras espécies intermediárias de enxofre ($S^{2-} \rightarrow S_x^{2-} \rightarrow S_nO_m^{y-}$, com x, n, m e y inteiros). A taxa de oxidação, para além de variar com a concentração de sulfureto, varia fortemente com a intensidade de corrente aplicada, sendo de ordem 2 para a densidade de corrente mais baixa, 10 mA cm^{-2}. Para densidades de corrente mais elevadas, em que o controlo de corrente é menos importante, a ordem de reação varia entre 0,15 e 0,44 para as densidades de corrente aplicadas de 20 e 60 mA cm^{-2}, respetivamente. Para a formação de SO_4^{2-}, a ordem da reação em relação à concentração de S^{2-} é sempre zero para todas as densidades de corrente aplicadas.

Nos estudos de remoção de contaminantes de efluentes da indústria dos curtumes, os desempenhos de cada ensaio de oxidação anódica foram verificados por meio de variações observadas nas concentrações de carência química de oxigénio, carbono inorgânico dissolvido, carbono orgânico dissolvido, carbono total dissolvido, azoto total Kjeldhal, azoto total, N-NH_4^+, N-NH_3, NO_3^-, NO_2^-, S^{2-} e SO_4^{2-}.

Para a oxidação eletroquímica de amostras de efluente não clarificadas (400 mL), os ensaios foram realizados com densidade de corrente de 30 mA cm^{-2}, agitação (100 rpm) e duração dos

ensaios de 8 h. O elétrodo de BDD apresentou o melhor desempenho na remoção de carbono orgânico dissolvido e de carbono total dissolvido. Os outros dois elétrodos testados apresentaram comportamentos semelhantes nas remoções do carbono orgânico dissolvido; Ti/Pt/SnO_2-Sb_2O_4 foi o menos eficiente na oxidação do azoto a NO_3^-, tendo levado à produção de formas de azoto gasoso, o que reduz a carga total de azoto presente nas amostras finais; o elétrodo de BDD removeu mais intensamente o S^{2-}, apesar dos outros elétrodos apresentarem um comportamento semelhante. O elétrodo de Ti/Pt/SnO_2-Sb_2O_4 foi mais eficaz na formação do SO_4^{2-}. Em relação ao consumo específico de carga, o BDD mostrou o menor consumo, 2,70 C/(g de CQO removida), contra 3,25 e 3,21 C/(g de CQO removida) para os elétrodos de Ti/Pt/PbO_2 e de Ti/Pt/SnO_2-Sb_2O_4, respetivamente.

Foram também realizados ensaios de oxidação anódica ao efluente clarificado e não clarificado. Para todos os ensaios de pré-tratamento por clarificação, o melhor desempenho foi verificado para a coagulação química. Isto parece ser devido ao melhor controlo operacional na coagulação química face à eletrocoagulação. Além disso, os catiões de ferro foram mais eficientes do que os catiões de alumínio. Isto é importante porque a clarificação por ferro evita a presença de alumínio no lodo final.

As oxidações anódicas das amostras (400 mL), clarificadas previamente por coagulação química ou eletrocoagulação por alumínio, foram processadas por 8 h com densidade de corrente de 30 mA cm^{-2} e agitação contínua (100 rpm). Foram realizados ensaios idênticos de eletro-oxidação para amostras não clarificadas. Neste sentido, a etapa de clarificação influenciou fortemente os processos de oxidação anódica e mostrou que a eletrodegradação com elétrodos de Ti/Pt/PbO_2 e Ti/Pt/SnO_2-Sb_2O_4 pode ser usada como etapa de polimento no tratamento de efluentes. O elétrodo de BDD, em geral, mostrou melhor desempenho na remoção de contaminantes a partir das amostras não clarificadas e foi muito eficiente na remoção S^{2-}, mas não na sua conversão em SO_4^{2-}. Pelo contrário, o elétrodo de Ti/Pt/SnO_2-Sb_2O_4 mostrou excelente desempenho para produção de SO_4^{2-} a partir de espécies intermediárias sulfuradas, uma vez que, para estes elétrodos, a formação de SO_4^{2-} foi maior do que a esperada. O consumo de energia dos processos de oxidação anódica realizados com ânodos de Ti/Pt/PbO_2 e de Ti/Pt/SnO_2-Sb_2O_4 é fortemente influenciado pelas concentrações de contaminantes. O processo combinado, coagulação química seguido por oxidação anódica com elétrodos de óxidos metálicos, provou ser uma boa alternativa aos elétrodos de BDD para tratamento de águas residuais. Um processo similar foi efetuado para amostras clarificadas, ou não, com catiões de ferro. Os resultados dos ensaios de oxidação anódica mostraram ser semelhantes aos observados quando a clarificação foi realizada por alumínio.

Tendo em vista os resultados anteriormente descritos, na última fase do trabalho efetuou-se a eletrooxidação, durante 8 h, de amostras clarificadas por catiões ferro, 0,25 g L^{-1}, com volume total de 2 L, em dois sistemas diferentes, dotados de recirculação: um sistema de eletrooxidação continha ânodos de Ti/Pt/SnO_2-Sb_2O_4 e de Ti/Pt/PbO_2 (A); o outro sistema era formado apenas por um ânodo de BDD (B). As densidades de corrente em cada conjunto foram

20 mA cm^{-2} e 40 mA cm^{-2} para Ti/Pt/SnO_2-Sb_2O_4 e Ti/Pt/PbO_2, respetivamente, no sistema A, e 60 mA cm^{-2} para o BDD, no sistema B. Ambos os sistemas testados mostraram um comportamento semelhante na remoção de CQO, carbono dissolvido total, carbono orgânico dissolvido, azoto total de Kjeldahl, N-NH_3 e azoto total. Os resultados mostraram a viabilidade dos elétrodos de óxidos metálicos em substituição do elétrodo de BDD em sistemas de oxidação; o conjunto A foi o menos eficiente na oxidação do azoto a NO_3^-, apesar de mostrar um comportamento semelhante ao conjunto B para a produção de azoto gasoso, o que reduz a carga total de azoto presente nas amostras finais; a concentração de CQO funcionou como um importante fator inibidor para a remoção azoto total de Kjeldahl. Em relação ao consumo de energia, de uma maneira geral, o conjunto B apresentou o menor consumo.

Palavras-chave

BDD; Ti/Pt/PbO_2; Ti/Pt/SnO_2-Sb_2O_4; Oxidação eletroquímica; Efluente de curtume; Oxidação de sulfureto.

ABSTRACT

Tannery wastewater is highly complex and contains high concentrations of organics and other toxic chemicals, such as sulfide and chromium, which inhibit the activity of microorganisms during biological oxidations and are not removed completely from wastewater. Since the biological processes are not able to fully depollute tannery effluents, other technologies, such as electrochemical oxidation processes, are being studied for the treatment of aqueous wastewaters.

In this work, the study of the electrochemical oxidation of samples from tannery wastewater, clarified or not, was carried out. Assays were run under galvanostatic conditions, with different current densities, in electrochemical reactors equipped with anodes based on metal oxides, Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4, and of boron-doped diamond (BDD). For the pretreatment by clarification, chemical coagulation (with iron and aluminum ions) and electrocoagulation (with iron and aluminum consumable anodes) were used. The performance of each assay was followed by variations observed in the concentrations of COD, DIC, DOC, TDC, TKN,TN, N-NH_4^+, N-NH_3, NO_3^-, NO_2^-, S^{2-} and SO_4^{2-}. The kinetics of the conversion of S^{2-} into SO_4^{2-} , in aqueous solutions of S^{2-} (60 mM), by electro-oxidation using a BDD electrode was also investigated.

For the conversion of S^{2-} to SO_4^{2-}, assays were run at current densities from 10 to 60 mA cm^{-2}, with a duration varying from 10 to 42 h. The results showed that the electrochemical conversion occurs in steps, via intermediate production of other sulfur species ($S^{2-} \rightarrow S_x^{2-} \rightarrow S_nO_m^{y-}$, with x, n, m and y integers) and the oxidation rate of the sulfide ion is dependent on its concentration and current density. The reaction order strongly varies with the applied current intensity, being order 2 for the lower applied current density. For higher applied current densities, where the current control is less important, the reaction order varies from 0.15 to 0.44 for the applied current densities of 20 and 60 mA cm^{-2}, respectively. For the formation of SO_4^{2-} from S^{2-} electro-oxidation, the reaction order with respect to sulfide varied from 0.35 to 0.05 when the applied current densities changed from 10 to 60 mA cm^{-2}.

The electrochemical oxidation for unclarified effluent samples under a current density of 30 mA cm^{-2} and in a batch with stirring (100 rpm) during 8 h assays showed the best performance for BDD electrode in the removal of COD and TDC. The others two tested electrode presented similar behavior in the DOC removal; Ti/Pt/SnO_2-Sb_2O_4 was the least efficient in the oxidation of nitrogen to NO_3^-, despite providing considerable production of gaseous nitrogen compounds, which reduces the total nitrogen load present in the final samples; removal of S^{2-} was more intense at BDD, although the other electrodes presented similar behavior. Ti/Pt/SnO_2-Sb_2O_4 electrode was more effective to form SO_4^{2-}. Regarding specific charge consumption, BDD showed the lowest consumption, 2.70 C g^{-1} of COD removed, against 3.25 and 3.21 C g^{-1} of COD for the Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 electrodes, respectively.

In all clarifications assays the best performance was verified for chemical coagulation. This appears be derived from a better operational control in chemical coagulation than in electrocoagulation. In addition, iron cation was more efficient than aluminum cation. This is important because the clarification by iron avoids the presence of aluminum in the final sludge

In the case of anodic oxidation (8 h assays, current density of 30 mA cm^{-2} and constant stirring at a rate of 100 rpm) for effluent samples (400 mL), previously clarified by chemical coagulation or electrocoagulation by aluminum, the clarification stage strongly influenced the anodic oxidation processes and showed that electrodegradation by Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 electrodes can be used as effluent polishing step. BDD electrode generally showed better performance in the removal of contaminants from the not clarified samples and was very efficient in the S^{2-} removal but not in its conversion to SO_4^{2-}. On the contrary, Ti/Pt/SnO_2-Sb_2O_4 electrode showed better performance in the production of SO_4^{2-} from intermediate sulfur species. The energy consumption of the anodic oxidation processes performed with Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 anodes is strongly influenced by the contaminant concentrations. The combined process, chemical coagulation followed by anodic oxidation with metal oxide electrodes, proved to be a good alternative to the BDD electrodes for wastewater treatment. The same situation was observed in the anodic oxidation of samples previously clarified by chemical coagulation or electrocoagulation using iron cation.

Finally, in the last stage, clarified samples by Fe^{3+} ion, 0.25 g L^{-1}, were submitted to anodic oxidation (8 h) in two different sets with recirculation system: set A composed by Ti/Pt/SnO_2-Sb_2O_4 + Ti/Pt/PbO_2 electrodes, and set B with BDD only. The current densities in each set were 20 mA cm^{-2} and 40 mA cm^{-2} for Ti/Pt/SnO_2-Sb_2O_4 and Ti/Pt/PbO_2, respectively, in set A; and 60 mA cm^{-2}, for BDD, set B. Both the tested sets showed similar behavior in the removal of COD, TC, DOC, TKN and ammonia nitrogen, showing the feasibility of metal oxides as electrodes in replacement to BDD electrode in anodic oxidation systems; set A was the least efficient in the oxidation of nitrogen to NO_3^-, despite show similar behavior to the set B for production of gaseous nitrogen compounds, which reduces the total nitrogen load present in the final samples; the COD concentration worked as an important inhibiting factor for TKN removal. Regarding energy consumption, in a general way, the set B showed the lowest consumption.

Keywords

BDD; Ti/Pt/PbO_2; Ti/Pt/SnO_2-Sb_2O_4; Electrochemical oxidation; Tannery wastewater; Sulfide oxidation.

SUMARY

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ACRONYMS

AO: Anodic Oxidation

BCS: Basic Chromium Sulfate

BOD: Biological Oxygen Demand

CC: Chemical Coagulation

COD: Chemical Oxygen Demand

DIC: Dissolved Inorganic Carbon

DOC: Dissolved Organic Carbon

DS: Dissolved Solids

EC: Electrocoagulation

EDS: Energy Dispersive X-ray Spectrometry

NTU: Nephelometric Turbidity Unit

SEM: Scanning Electron Microscope

SS: Suspended Solids

SC: Specific Charge Consumption

SHE: Standard Hydrogen Electrode

TDC: Total Dissolved Carbon

TKN: Total Kjeldahl Nitrogen

TN: Total Nitrogen

TS: Total Solids

1 INTRODUCTION

The tanning industry converts animal hides to leather, a material relatively stable and non-degradable. The transformation of hides/skins into leather involves three main stages: the beamhouse, where the skins are cleaned and all the undesirable substances are removed; the tanning process, where the pretreated skins are transformed into leather; the finishing process that gives the wanted physical and mechanical properties to the leather.

The leather industry is one of the oldest industries in the world and tannery effluents are a source of hazardous environmental impacts. The characteristics of tannery wastewater vary widely and are dependent on the adopted tanning process, the amount of water used, the process of hide preservation, and the hide processing capacity. Tannery wastewater is a powerful pollutant that can cause severe environmental problems because of its high organic and inorganic loads, suspended solids, and high contents in chromium, chloride, ammonia, sulfide, oil, grease, among others.

Biological processes are often used to treat tannery wastewater. However, the application of these processes to treat tannery effluents presents some difficulties due to their composition. Thus, conventional biological treatment methods are often inadequate to completely remove pollutants present in tannery wastewater. Considering the complexity of the effluents generated by tanneries, and the serious environmental and technological problem posed by this industry, the development of effective treatment methods for these effluents is extremely necessary.

Electrochemical oxidation processes have already been tested for the treatment of different types of complex wastewaters (Cabeza et al., 2007; Costa et al., 2008; Isarain-Chávez et al., 2014; Rao et al., 2001; Panizza et al., 2010; Fernandes et al., 2014). In this context, the main objective of this work was to evaluate and compare the efficiencies of different electrode materials, Ti/Pt/PbO_2, Ti/Pt/SnO_2-Sb_2O_4 and BDD, in the removal of carbonaceous and nitrogenous compounds from tannery effluents, by electrodegradation processes. Since coagulation is by far the most widely used process for wastewater pretreatment, this work intended also to study the electrodegradation of tannery effluents pretreated with chemical coagulation or electrocoagulation, with iron or aluminum ions.

Sulfide and chromium are two of the most hazardous pollutants present in tannery effluents. Thus, this work was also focused on the removal of these contaminants during the proposed treatment, and the kinetics of sulfide removal in the form of sulfate was also studied, as well as the influence of the clarification of the sample by chemical coagulation and electrocoagulation on the sulfide and chromium removals.

This Ph.D thesis is structured in five chapters. This first one reports an initial overview of the present work. Chapter 2 presents a broader approach of the literature review, including the characterization of the main stages of leather production, effluent generation, and common treatments of the generated effluent and new procedures that can be applied for this purpose. Materials and methods used to monitor the removal of various contaminants present in samples from tannery industry are described on chapter 3. According to the present work goals, chapter 4 was subdivided into different sections reporting the experimental procedure applied, the samples preliminary treatment, the realization of anodic oxidation assays, the results and conclusions.

The sections present on chapter 4 are structured as:

4.1 – In this section it is presented the study performed to evaluate the effect that current density has on the conversion of S^{2-} to SO_4^{2-} during the anodic oxidation of aqueous solutions of Na_2S with the monitoring of changes in concentrations of S^{2-} and SO_4^{2-} after defined periods of time. BDD electrode was used as anode.

4.2 – This section presents the studies done to evaluate the performance of three different anodes, Ti/Pt/PbO_2, Ti/Pt/SnO_2-Sb_2O_4 and BDD, on the decrease of organic and nitrogenous matter and S^{2-}. In order to conduct this study, anodic oxidation tests were performed on leather industry effluents. These tests include the monitoring of contaminants concentration variation after defined periods of time and energy consumption for some contaminants.

4.3 and 4.4 – Following the results of the performances of the different electrodes utilized in section 4.2, in these two sections, the results obtained in the anodic oxidation assays carried out with the three electrodes are presented. The samples used in these studies were previously clarified by chemical coagulation or electrocoagulation, using iron or aluminum as clarification agents. The effect of the pretreatment (clarification) on the anodic oxidation process was evaluated considering the dynamic of contaminants removal and the energy efficiency of the process. An evaluation of the performance of each clarification agent in the pretreatment was also reported.

4.5 – Results from sections 4.3 and 4.4 were used as a reference for the implementation of the studies presented in this section. Therefore, two sets of anodic oxidation were assembled with different combinations of electrodes and recirculation of the effluent. Regarding the anodic oxidation assays, the samples were previously clarified by chemical coagulation using iron cations. In this case, the performance of each system also was evaluated based on the dynamic removal of contaminants and energy consumption.

The main conclusions and the prospects for future work are presented in chapter 5.

2 LITERATURE REVIEW

This chapter starts with a description of the leather production process from raw fur and all the environmental constrains of the tanning industry. An outline of the tanning process and the implication on the characteristics and the main contaminants of the effluents is also presented. The usual methods to treat tannery effluents and other less common treatment technologies, such as chemical and electrochemical coagulation, are also discussed. The chapter ends with an overview on recent proposals for pollution abatement – anodic oxidation with boron-doped diamond and metal oxide anodes.

2.1 Tanning Industry

Leather has remained a unique material for a long time. However, on account of the environmental threat from the tanning activity, it has changed from an ecologic to a negative product, for the public perception (Sreeram and Ramasami, 2003). Leather tanning industry is considered one of the most polluting industrial activities in the world (Mannucci et al., 2010). The ecological degradation arising from traditional techniques of leather processing has been well-documented (Rao et al., 2003).

The leather production involves leather/skin cleaning of unwanted material through a series of pre-tanning operations, a permanent preservation through tanning, and incorporation of aesthetic characteristics during post-tanning steps (Suthanthararajan et al., 2004). Tanning operations consist of transforming the raw hide/skin, a highly putrescible material, into leather, a stable product with a commercial value (Ayoub et al., 2013). The leather production process includes different steps, in which large quantities of water and chemicals are applied to the skins.

The transformation of skins into leather involves three main stages: a) beamhouse, which eliminates the substances that will not compose the leather; b) tanning, where the pretreated skins are transformed into leather; c) finishing that confers to the leather the desired physical and mechanical properties (Costa et al., 2008; Mlaik et al., 2011; El-Sheikh et al., 2011).

The first phase of the hides processing is called beamhouse operations and involves multiple mechanical, chemical and biological unit operations. Its objective is to remove dirt, hair, epidermis, non-collagenous proteins and grease from raw skin, and open up the collagen fibers to favor the subsequent tanning process (Wang et al., 2016). The process is performed in a drum by mixing the raw hides with an alkaline solution containing lime and reducing agents, usually sulfide salts, being the hair chemically removed from the surface of the hide (Şengil et al., 2009). The beamhouse operations are the most water consuming and the

effluents generated present very high organic load (Mendoza-Roca et al., 2010). The dehairing procedures are known for its uncleanness, contributing with 60 to 70% of the total pollution load in leather production. The conventional dehairing process with sodium sulfide and lime contributes to a significant amount of BOD, COD, sulfide, and solid wastes (Senthilvelan et al., 2012).

The tanning process is one of the oldest procedures in the world, and currently these industrial activities are based on chemical processes involving several organic and inorganic compounds (Paschoal et al., 2009). This step gives the leather stabilization and durable finish. The stabilization of the collagen matrix proteins in the skin against the wet and dry heat, mechanical stress, enzymatic attack, among others, forms the basis of leather production. According to Walsh and O'Halloran (1996), and Sreeram and Ramasami (2003), this stabilization is attributed to the formation of new chemical crosslinks in the matrix proteins.

The tanning stages are classified as mineral, vegetable and synthetic. When the skin stabilization is achieved by a suitable inorganic salt, the process is known as mineral tanning, and the most commonly used mineral tanning salt is the basic chromium sulfate, BCS (Sreeram and Ramasami, 2003). According to Ram et al. (1999), 90% of the leather is produced by the chrome tanning process. The BCS is mainly a mixture of $Cr(OH)SO_4$ and Na_2SO_4, characterized as a green colored powder containing Cr_2O_3, 26%, and $Na_2(SO_4)$, < 26%, with 33% of basicity. This means that the BCS is one-third basic with respect to basicity of $Cr(OH)_3$ (Panda et al., 2016).

The finishing step complements the previous stage, tanning, and provides the leather with the required physical and mechanical properties, such as color, tensile strength, impermeability, softness, flexibility and elasticity.

In the different steps of the leather production process large quantities of water and chemicals are applied to the skins, being the type of chemicals dependent on the applied processes. Thus, the characteristics and the flow rate of the effluent are not constants. The literature data are not accurate about the water quantity used by the leather industry, and it can vary between 15 and 20, 30 and 35, 30 and 40, and 25 and 80 m^3 of water/ton of processed skin, according to Mohammed and Sahu (2015), Sreeram and Ramasami (2003), Rao et al. (2003) and Mannucci et al. (2010), respectively. However, according to Chowdhury et al. (2013), 90% of the consumed water is discharged as effluent.

2.2 Characteristics of the tannery industry effluent

The tannery wastewater is a powerful pollutant that can cause severe problems associated with its organic load, inorganic matter, chromium, suspended solids, organic and ammoniacal nitrogen, sulfide, chloride, among others, derived from the matter removed from raw

hides/skins and from reagents added for processing these materials (Roš and Gantar, 1998; Szpyrkowicz et al., 2001; Szpyrkowicz et al., 2005; Kongjao et al., 2008; Zhi et al., 2009; Aber et al., 2010; Ayoub et al., 2011; Chowdhury et al., 2013; Gallego-Molina et al., 2013). Thus, leather industry has a profound impact on the environment because it generates large amounts of wastewater, becoming an important source of industrial wastewater and a serious threat to the aquatic environment and the human health (Szpyrkowicz et al., 2005; Tammaro et al., 2014).

According to Kurt et al. (2007), the characteristics of the effluent from tannery can vary widely depending on the nature of the tanning process adopted, the amount of water used, the skins conservation process, the ability of processing, among others. In fact, a wide variety of constituents may be found in raw effluent of tannery, besides disparate physicochemical characteristics. This wide range in the composition of tannery effluents is well documented in Table 1 that gives an overview on the composition of different effluents from leather industry presented in the literature.

In the next sections, details about some contaminants present in tannery effluents will be presented.

Table 1. Composition* of raw wastewater from the leather industry according to different literature references

pH	BOD_5	COD	SS	DS	TS	Cl^{1-}	S^{2-}	SO_4^{2-}	Cr^{3+}	Cr total	TKN	$N\text{-}NH_3$	$N\text{-}NH_4^+$	Conductivity	Reference
7.4	1,470	3,700	2,690			6,520	440			22		180		21.63	Apaydin et al., 2009
3.2		13,500	5,800				90		2,889				1,016		El-Sheikh et al., 2011
7.2	910	2,810	1,520			6,400	89			62		130		19.95	Kurt et al., 2007
8	2,000	5,250	3,000		20,000	7,750				175					Rao et al., 2003**
7.1	2,400	17,500	18,500			4,500	80	2,200					185		Mannucci et al., 2010**
7.5	920	3,980	6,800	14,000	20,800			4,000		9.81				18.65	Chowdhury et al., 2013**
8		11,000	5,500			14,750	164.7	4,000					198.5	20	Panizza and Cerisola, 2004**
8.6	977	2,533	12,44	21.6		6,528	860			258		118		20	Mandal et al., 2010
9.1		2,487											128		Szpyrkowicz et al., 1995**
10.5	1,126	3,114	1,147	17,737	18,884	8,392	55			83		33			Ram et al., 1999
10.7	2,906	11,153		6,810			507			32.9	1,350		162		Leta et al., 2004**
7.9	802.5	5,400	777.5	16,500						12.9	157				Kongjao et al., 2008**
7.7		2,426					286			29.3			335		Szpyrkowicz et al., 2005**
6.6	1,150	2,700	490								76.5		35		Di Iaconi et al., 2010**
8.5	774.9	2,442	1,232	8,265		3,067	156	1,246		68	118				Haydar and Aziz., 2009a**

* Conductivity is in mS cm^{-1}; all other parameters, except pH, in mg L^{-1}.
** Medium values

2.2.1 Sulfide

The first step of leather production is the dehairing. As the conventional dehairing process is performed with sodium sulfide and lime, the beamhouse effluent contains high concentration of sulfide ions (Murugananthan et al., 2004; Şengil et al., 2009; Mendoza-Roca et al., 2010; Senthilvelan et al., 2012). At the end of the operation, a residual bath with a pH value of about 12 and with a high content of organic substances (proteins), lime and sulfur compounds (as S^{2-} and HS^{-}) is left (Mendoza-Roca et al., 2010).

Sulfide is toxic, odorous and corrosive and is of particular concern in sewer systems, since it causes pipes corrosion (Cai and Zheng, 2013). Concrete corrosion problems have also been reported for S^{2-} concentration between 0.1 and 0.5 mg L^{-1} (Zhang et al., 2008). Its presence in sewage systems is a common problem due to the stimulation of the metabolic activity of sulfate-reducing bacteria, given the high organic load and low dissolved oxygen concentration (Garcia-de-Lomas et al., 2007).

In leather tanning industrial areas sulfide management represents a major problem (Vannini et al., 2008). The extensive use of sulfide bears unfavorable consequences on the environment and on the efficacy of effluent treatment systems (Senthilvelan et al., 2012).

Sulfide toxicity is a common problem for anaerobic treatment systems of industrial waste (Wang et al., 2014b). The presence of sulfide ions in the liquid phase can cause several problems in plants of conventional activated sludge, such as inhibition of nitrification, growth of filamentous bacteria, floc disruption, as well as lower efficiency in sludge dehydration (Vannini et al., 2008). Thus, beamhouse wastewater presents a great problem in the anaerobic treatment due to the high content in sulfide and organic sulfur that, although in a low concentration, will become sulfide during the anaerobic treatment (Schenk et al., 1999).

The soluble sulfide concentration varying from 50 to 100 mg L^{-1} can be tolerated by anaerobic treatment systems; with continuous operation and some acclimation, concentration up to 200 mg L^{-1} of soluble sulfides can be tolerated with no significant inhibition of the anaerobic treatment (Vijayaraghavan and Murthy, 1997). However, at a pH near neutral, sulfides at concentrations above 200 mg L^{-1} are toxic to the methane-forming bacteria in anaerobic systems (Song et al., 2001).

2.2.2 Chromium

The chrome tanning method is widely used in the majority of the tanneries, through the application of chromium salt, although the vegetable tanning method may also be applied (Tahir and Naseem, 2007). According to Bajza et al. (2004), chrome tanning accounts for 70 to 80% of all leather production, given the outstanding tanning properties of the trivalent chromium ion.

The leather tanning with Cr(III) was first introduced in 1858 (Walsh and O'Halloran, 1996). Although the tanning based on chrome presents advantages such as high processing rate, low costs and a greater stability of the produced leather, about 20 to 40% of the added chromium do not react with the skins and remains in the final effluent (Houshyar et al., 2012). The effluent from the chrome tanning process consists mainly of a chromium saline solution, with a pH between 3 and 5 (Dantas Neto et al., 2004).

According to Cooman et al. (2003), the chrome tanning wastewater contains high concentration of total chromium (up to 4,950 mg L^{-1}). In the industrial area, the chrome tanning wastewater stream is usually homogenized with the remaining industrial effluents and the chromium precipitates as chromium hydroxide, thus being retained in the sludge of the water treatment plants (Mohammed and Sahu, 2015).

The leather industry contributes with 40% of industrial pollution by chromium (López-Luna et al., 2009). Although most of the tanning operations in leather industry is based on Cr(III), attention is focused on the possible hazards resulting from the presence of Cr(VI) in the effluent, due to the natural oxidation or biotransformation in the environment (Paschoal et al., 2009). The Cr(VI) is much more mobile than Cr(III), more difficult to remove from solution, and the most toxic form of chromium, about 10 to 100 times more toxic than Cr(III) (Guertin et al., 2005).

Cr(III) is by far the most stable chromium oxidation state, and this is reflected in the high oxidizing power of Cr(VI), Cr^{6+}/Cr^{3+} (E^o= 1.33 V) (Greenwood and Earnshaw, 1997). However, the inter-conversion between Cr(III) and Cr(VI) is strongly dependent on the environmental nature (Sirajuddin et al., 2007). Moreover, although the thermodynamic indicates that Cr^{6+} is present under oxic conditions, and Cr^{3+} predominates under anoxic or suboxic conditions, both forms have been detected simultaneously, and one possible explanation is the slow kinetics of reactions between Cr^{6+} and reducing substances (Sedlak and Chan, 1997).

Although biological processes are usually prescribed for treating industrial effluents, the high level of chromium may exert toxic or inhibitory effects on the microorganism activities (Dogruel et al., 2006; Houshyar et al., 2012; Lofrano et al., 2013). In fact, Stasinakis et al. (2002) found a significant inhibition of heterotrophic growth for Cr(VI) concentration of 10 mg L^{-1}. Farabegoli et al. (2004) reported inhibition of nitrifying bacteria when Cr(III) reached 120 mg L^{-1}. Leta et al. (2004) found reductions of nitrification activities when the Cr(III) concentration reached 50 mg L^{-1}.

2.2.3 Organic load

The tannery wastewater is a complex mixture of biogenic matter of the hides and a large variety of organic chemicals added during the tanning process that contains high concentrations of dissolved organic matter and suspended solids (Reemtsma and Jekel, 1997;

Lefebvre et al., 2006). The organic matter is mainly due to blood, dung, proteins in solution and in suspension, animal fats, lipids and hair from the raw skins. In fact, the raw skin loses about 30% of the organic material during the production of the leather (Mannucci et al., 2010). The organic matter may also be introduced during the working cycle, by the use of tannins in the tanning process, or the use of organic solvents in the leather degreasing (Cassano et al., 2001). Thus, according to the process utilized, effluents present a complex and variable matrix (Ates et al., 1997). Rao et al. (2001) found the presence of various organic compounds, namely, phenol, pelletierine, 5-benzoyloxy benzoic acid, dibutyl phthalate, among others, in the raw wastewater.

The beamhouse operations generate the principal organic load in leather industry, but are not the only source. In fact, the retanning and wet finishing streams are relatively low in BOD and TSS, but contain high COD concentration, in addition to trivalent chromium, tannins, sulfonated oils and spent dyes (Lofrano et al., 2013).

Although COD is a useful parameter that reflects the total organic content of a wastewater, it has inherent deficiencies because it covers not only biodegradable organics but also biologically resistant and refractory compounds, i.e., it provides no information on significant organic fractions with different biodegradation kinetics. Despite this, some information about the different forms of organic load were collected in the literature: Orhon et al. (1999) found in the settled tannery wastewater that, from the total COD, 79% were biologically degraded (19% readily, and 60% slowly biodegradable), and the residual 21% were biologically refractory; Karahan et al. (2008), working with tannery wastewater, found that 60, 25 and 15% of the total COD were particulate fraction, soluble, and colloidal fraction, respectively.

Previous studies have reported that tannery wastewaters include biodegradable portions comprising different fractions with distinct biodegradation rates and inert COD fractions that play an important role on the extent of treatment performance (Ates et al., 1997; Orhon et al., 1998). Thus, the BOD is a controversial parameter if applied to tannery wastewater since the wastewater contains many inhibitors (Ates et al., 1997).

For leather industry that uses non-chrome tanning, the tanning stage is performed with tannins, i.e., there is one more problem for the organic load. The tannins are polyphenolic compounds characterized by low biodegradability (Szpyrkowicz et al., 2005). They are difficult to break and are considered highly toxic pollutants (Vlyssides and Israilides, 1997). Tannins form stable complexes with protein, thus making it resistant to microbial decomposition (Vijayaraghavan and Murthy, 1997). Some groups of tannins have complex structures, which are not easily degraded by microorganisms in either aerobic or anaerobic environments (Mingshu et al., 2006). Methanogens bacteria are strongly inhibited by tannins concentration between 0.3 to 2 g L^{-1} (Gupta and Haslam, 1980).

For the reasons presented above and because conventional biological processes are not capable of the complete removal of these compounds, tannery wastewater is among the most

difficult wastes to treat and is a serious and actual technological and environmental challenge (Vlyssides and Israilides, 1997; Costa et al., 2008; Schrank et al., 2009).

2.2.4 Nitrogenous matter

The predominant nitrogen fraction in tannery wastewaters is organic nitrogen from non-collagenous proteins (such as keratin, albumins, globulins, etc.) that are removed from skin during beamhouse processing (Leta et al., 2004; Wang et al., 2016). The total nitrogen in the beamhouse effluent is mainly organic nitrogen (60%) and ammonia nitrogen (40%), being nitrate and nitrite negligible (Wang et al., 2012). According to the same authors, the contamination by ammonia nitrogen is mainly originated from deliming and bating processes, due to the use of ammonium salts that accounts for 80% of ammonia nitrogen pollution in the beamhouse wastewater.

The elimination of solubilized proteins would considerably reduce the organic nitrogen content, but the treatment of tannery wastewater with high organic and nitrogen contents by conventional biological processes, such as activated sludge, is not very economical nor technically feasible, as these processes normally require large area and high operating cost (Marsal et al., 2010; Chung et al., 2004). The presence of sulfide, chromium and especially chloride are likely to exert adverse effects on nitrification. Furthermore, fluctuations in wastewater temperature become a major concern for maintaining a nitrifying biomass (Murat et al., 2006). According to Orhon et al. (2000), the high chloride content of the wastewater should be the major concern for the inhibition of the nitrification process, thus acting as the limiting step for nitrogen removal.

The biological treatment is commonly used for tannery wastewater treatment (Szpyrkowicz et al., 2001). However, according to Murat et al. (2002), the nitrogen removal from tannery wastewater by biological treatment is more complex, since ammonium oxidizing bacteria are difficult to maintain in the reactor biomass due to the high conductivity and the presence of inhibiting substances. The limiting step for nitrogen oxidation is nitrification, a process which is sensitive to inhibitory effects (Orhon et al., 1999).

In conventional biological treatment, the mass ratio of C:N:P is one of the most important factors for achieving efficient removal of pollutants (Wang et al., 2016). The proper ratio of C:N:P is, generally, around 100:5:1 and 250:5:1 for aerobic and anaerobic treatments, respectively (Ammary, 2004). Tannery wastewater contains excessive nitrogen concentration and, therefore, conventional biological treatment usually achieves unsatisfactory nitrogen removal (Sathish et al., 2013; Zhou et al., 2014). According to Wang et al. (2016), total nitrogen concentration in untreated wastewater is commonly higher than 200 mg L^{-1}.

Due to the high ammonium content in tannery wastewater, it cannot be removed by conventional nitrification and denitrification, and preliminary ammonium removal is

considered as a prerequisite for the application of biological processes (Min et al., 2004). Nevertheless, a considerable quantity of ammonium nitrogen will be formed from organic nitrogen during biochemical treatment of tannery wastewater, resulting in the decrease of ammonia removal rate.

2.3 Usual methods for wastewater treatment

To reduce the organic content from industrial effluents biological processes are usually recommended (Lofrano et al., 2013). In the case of tannery general effluents, they are usually pretreated by mechanical and physico-chemical processes, followed by biological treatment (Bordes et al., 2015; Gomes et al., 2016). As already pointed out, biological processes are often inefficient and inadequate to remove pollutants completely, besides being time-consuming (Apaydin et al., 2009). In the case of tannery effluents, very often they present low biodegradability, since the ability of some microorganisms to degrade some contaminants is restricted, which does not allow the complete removal of these compounds by a conventional biological process (Szpyrkowicz et al., 2005; Costa et al., 2008; Benhadji et al., 2011). In fact, data presented in Table 1 shows only one effluent with a BOD/COD ratio higher than 0.40 (Di Iaconi et al., 2010).

According to Reemtsma and Jekel (1997), the biological treatment of tannery effluents in two steps, aerobic and anaerobic, tends to promotes enrichment of high-molecular weight compounds, which can act as recalcitrant agents in the process. In addition, composition, temperature, pH, COD, suspended solids, among others, fluctuate significantly with the tanning procedure, leading to unsatisfactory performance of the conventional biological treatments (Farabegoli et al., 2004; Wang et al., 2014b; Deghles and Kurt, 2016). Furthermore, the presence of sodium sulfide (for the dehairing process) and chromium (from the tanning process) are potentially toxic for the posterior biological treatment of the wastewater (Song et al., 2001; Karthikeyan et al., 2012; Senthilvelan et al., 2012).

Biological sulfide oxidation under aerobic conditions is exhaustively used, but the oxygen injection requires energy which makes the operation costly (Tang et al., 2010). On the other hand, biological sulfide oxidation under anaerobic conditions presents problems like odor, among others. Anyway, this process is suitable only to low sulfide concentration (Alcántara et al., 2004). In fact, sulfide is known to be toxic to anaerobic bacteria, leading to complete inhibition of anaerobic step for sulfide concentration higher than 260 mg L^{-1} (Schenk et al., 1999; Song et al., 2001).

After beamhouse, if the tanning process is chrome based, the effluent is chrome-rich, which can generate problems for the biological treatment. According to Lofrano et al. (2013), the presence of metals, like chromium, can inhibit this treatment process. In fact, there is a significant inhibition of heterotrophic growth for Cr(VI) concentration around of 10 mg L^{-1},

and inhibition of nitrifying bacteria when chromium concentration reached 120 mg L^{-1}, as well as reductions in the nitrification activities when the Cr(III) concentration reached 50 mg L^{-1} were already reported (Stasinakis et al., 2002; Farabegoli et al., 2004; Leta et al., 2004).

Thus, alternative approaches to classical physico-chemical and biological processes to treat tannery effluents are being increasingly explored (Bordes et al., 2015; Isarain-Chávez et al., 2014). The main alternatives are based on basic physical treatment, chemical treatment, including coagulation/flocculation (Garrote et al., 1995; Roš and Gantar, 1998; Ayoub et al., 2000; Haydar and Aziz, 2009b; Ayoub et al., 2011; Islam et al., 2011; Chowdhury et al., 2013), electrocoagulation (Murugananthan et al., 2004; Kongjao et al., 2008; Apaydin et al., 2009; Șengil et al., 2009; Tchamango et al., 2010; Isarain-Chávez et al., 2014; Deghles and Kurt, 2016), biological treatment (Vijayaraghavan and Murthy, 1997; Roš and Gantar, 1998; Sekaran et al., 2013), combined chemical/biological processes (Roš and Gantar, 1998; Song et al., 2000; Song et al., 2001; Di Iaconi et al., 2002; Song et al., 2004; Ryu et al., 2007), electrochemical treatment (Szpyrkowicz et al., 1995; Rao et al., 2001; Szpyrkowicz et al., 2005; Costa et al., 2008; Sundarapandiyan et al., 2010; Isarain-Chávez et al., 2014), ion exchange (Tiravanti et al., (1997), ozonization (Preethi et al., 2009; Houshyar et al., 2012), and Fenton (Thankappan et al., 2015), among others.

2.4 Additional methods for wastewater treatment

Since the tannery wastewater contains high amount of suspended solids and possesses high turbidity, coagulation processes can be a good alternative to treat this type of effluents. In this section, the treatment of this type of wastewaters by chemical coagulation and electrocoagulation processes, using iron and aluminum ions abilities, will be discussed.

2.4.1 Chemical Coagulation

The stability of a pollutant is determined by its physical chemical properties. Many pollutants are made of particles with the same electric charge that repel each other and create a stable system (colloid system) (Holt et al., 2002). Settling rates of colloid forms are so slow that remove them from the wastewater by simple sedimentation is impossible, and a coagulant agent must be applied (Corbitt, 1989).

Coagulation is an event in which the charged particles in colloidal suspension are neutralized by counter-ions, through mutual interaction, forming agglomerates and sedimenting (Mollah et al., 2001). The destabilization, followed by coagulation → flocculation → sedimentation can be achieved by cations that interact specifically with negative colloids to neutralize their charge. Coagulation may involve two distinct mechanisms: (i) neutralization of the negative charges of the colloids by hydrolysis products and (ii) incorporation of impurities in the

amorphous hydroxides (Bajza et al., 2004). The contaminants destabilization mechanism may be as follows: (i) compression of the diffuse double layer of charged species by the interactions with counter-ion from coagulants; (ii) neutralization of the ionic species present in the wastewater, reducing the electrostatic repulsion and initiating the clotting; (iii) formation of flakes with capture of the contaminants particles and subsequent removal of contaminants by sedimentation (Mollah et al., 2001).

The chemical coagulation (CC) process consists of the rapid dispersal of a coagulant by intense agitation (rapid mixing), followed by non-intense agitation (slow mix) and sedimentation. Although widely applied for effluent clarification, this treatment is influenced by the characteristics of the raw water, temperature, pH, type of coagulant, coagulant dosage, rapid mixing intensity and its duration time (Rossini et al., 1999).

According to Alley (2007), the coagulant dosage can be: a) insufficient to promote coagulation; b) enough to destabilize colloids by reduction of its negative surface charges, in a neutral or weakly acidic conditions; c) excessive, with reversal of the electric charges of the colloids, rebalancing the particles; d) excessive with super saturation and metal hydroxide precipitation scavenging colloidal particles, in neutral or alkaline conditions.

About the rapid mixing stage, Dharmappa et al. (1993) found that this is the most significant step for process optimization. Nevertheless, the literature suggests conflicting recommendations for rapid mixing times: whereas some authors suggest instant mix based on chemical theories of adsorption-destabilization, others recommend several minutes to detention times in rapid mixing units (Rossini et al., 1999).

The treatment of effluent by coagulation-flocculation is applied to all kinds of industries but is particularly important for tannery industry, since it contains high organic load. A substantial part of these pollutants can be removed at coagulation-flocculation-sedimentation pretreatment (Haydar and Aziz, 2009c). In fact, CC is by far the most widely used way to remove substances responsible for water turbidity (Song et al., 2004).

Although there is sludge formation during CC, this sludge is an organic mass (biosolid) and can be applied as fertilizer to enrich the agricultural soil after being treated and stabilized (Bengtsson and Tillman, 2004; Axelrad et al., 2013).

Metal salts are widely used as CC and play a vital role in the removal of many impurities from polluted waters. The most common additives are aluminum sulfate, ferric chloride and ferric sulfate (Duan and Gregory, 2003).

2.4.1.1 Chemical coagulation by aluminum salts

Hydrolyzing coagulants have been applied routinely since the beginning of the 20th century and play a vital role in the removal of several impurities from polluted waters (Duan and Gregory, 2003). When promoted by aluminum salts, the action mode is explained by the

neutralization of the negative charges on the colloids' surface by hydrolysis products like $AlOH^{2+}$ and $Al(OH)_2^+$, Eq. (1) and (2), and incorporation of impurities by the formed hydroxide like $Al(OH)_3$, Eq. (3), (Holt et al., 2002).

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+ \quad (1)$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (2)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad (3)$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad (4)$$

Table 2 lists some results obtained in the treatment of tannery effluents by chemical coagulation using aluminum salts as coagulant.

Table 2. Results presented in the literature for removal of COD, S^{2-} and TKN from tannery wastewaters by chemical coagulation using aluminum salts.

Treatment	Parameter	C_0 / mg L^{-1}	$Al^{3+}_{(ad)}$ / mg L^{-1}	pH	Removal / %	Reference
Chemical Coagulation	COD	8080	2300	3.1	68.3	Das et al., 2007[a]
		6650	3.99	6.8	80.0	Islam et al., 2011[a]
		3300	88.8	7.5	32.0	Song et al., 2001
		3300	88.8	7.0	36.0	Song et al., 2004
		1840	18.9	7.5	58.7	Haydar and Aziz, 2009b
	S^{2-}	100	88.8	7.5	80.0	Song et al., 2001
	TKN	820	88.8	7.5	40.0	Song et al., 2001

C_0= initial concentration of the considered parameter;
$Al^{3+}_{(ad)}$= initial aluminum cation concentration added.
[a]= the clarifier agent "Alum" present in Das et al., 2007, and Islam et al., 2011, was considered as $KAl(SO_4)_2 . 12H_2O$

Data in Table 2 illustrate the situation previously described, and the different initial pH and organic loads may explain the different Al^{3+} optimized concentrations used to clarify the samples, which produced different removals rates of the considered parameters.

About the effect of pH, the loss of removal efficiency in Das et al. (2007) appears to be derived from the low pH value of 3.12, since, according to Alley (2007), the optimal pH range for clarification by aluminum is between 5 and 7. Furthermore, considering that the results were obtained from different tannery wastewater, the literature data do not identify the best $[COD]/[Al^{3+}]$ ratio to maximize COD removal.

Regarding S^{2-} and TKN removals, the work performed by Song et al. (2001) shows that the removals of these two parameters are also satisfactory. Although S^{2-} can be removed by

addition of Al^{3+} cations, its removal tends to be less efficient, if compared with the removal by Fe^{3+} cations. This situation can be explained on the basis of the solubility product (K_{sp}) of the possible species formed from S^{2-} with Al^{3+}, Al_2S_3, Eq. (5) (Freiser, 1992), or with Fe^{3+}, Fe_2S_3, Eq. (6) (Brown and Holme, 2011). Thus, better S^{2-} removal is expected with iron cations, since iron sulfide is much more insoluble than aluminum sulfide.

$$Al^{3+} + S^{2-} \rightarrow Al_2S_3 \qquad k_{sp}= 2.0x10^{-7} \qquad (5)$$

$$Fe^{3+} + S^{2-} \rightarrow Fe_2S_3 \qquad k_{sp}= 1.4x10^{-88} \qquad (6)$$

2.4.1.2 Chemical coagulation by iron salts

According to Mollah et al. (2001), in the case of CC by $FeCl_3$, the Fe^{3+} released may undergo hydration and, depending on the pH of the solution, can produce species such as $Fe(OH)^{2+}$ and $Fe(OH)_2^{+}$, through Eq. (7) and (8), which are responsible for the neutralization of the pollutants surface charges and their subsequent removal. Moreover, due to the formation of insoluble gelatinous species, $Fe(OH)_3$, Eq. (9), part of the suspended material is removed during the sedimentation process.

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^{+} \qquad (7)$$

$$Fe^{3+} + 2\ H_2O \rightarrow Fe(OH)_2^{+} + 2\ H^{+} \qquad (8)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^{+} \qquad (9)$$

Similar situation may occur when Fe^{2+} is the coagulant agent because there may be formation of $Fe(OH)_2$ or $Fe(OH)_3$. This latter is more common for systems with a high pH.

Table 3 lists COD, S^{2-} and TKN removals from tannery effluents by CC using iron salts as coagulant. As the concentrations of the contaminants are not unique and depend on the different steps, water quantity and chemicals applied to the skins production, the different Fe^{2+} and Fe^{3+} concentrations utilized in samples clarifications and the different removal rates obtained were expected.

According to Aboulhassan et al. (2006), $FeCl_3$ proved to be an effective coagulant in the pH range between 7 and 9. However, when comparing the works of Chowdhury et al. (2013), Song et al. (2001 and 2004) and Garrote et al. (1995), with similar pH values and COD concentrations, there is no obvious tendency in the COD removal rate with iron cation concentration. Furthermore, if all the values presented in Table 3 are compared, it is clear that there is no relationship between COD and Fe^{n+} added, like $[Fe^{n+}]/[COD]$, that provides an ideal clarifier dosage and COD removal, i.e., the coagulation performance depends of the

inherent characteristics of the effluent, and is difficult to identify the best $[Fe^{n+}]/[COD]$ ratio that maximizes COD removal.

Table 3. Results presented in the reading for removal of COD, S^{2-} and TKN from tannery wastewaters by chemical coagulation using iron cations.

Treatment	Parameter	C_0 / mg L^{-1}	$Fe^{n+}_{(ad)}$ / mg L^{-1}	pH	Removal / %	Reference
Chemical Coagulation	COD	3,980	51.7	7.0	92.4	Chowdhury et al., 2013
		3,300	165.6	7.5	35.6	Song et al., 2001
		9,000	34.4	12.9	64.8	Ryu et al., 2007
		6,650	24.1	10.4	80.0	Islam et al., 2011
		3,300	165.6	7.0	36.0	Song et al., 2004
		3,192	68.9	8.5	86.0	Garrote et al., 1995
		5,840	957.9	5.5	67.0	Zhi et al., 2009
	S^{2-}	100	165.6	7.5	100	Song et al., 2001
		625	957.9	5.5	99.0	Zhi et al., 2009
	TKN	610	34.4	12.9	36.8	Ryu et al., 2007
		820	165.6	7.5	47.6	Song et al., 2001

C_0= initial concentration of the considered parameter;
$Fe^{n+}_{(ad)}$= Fe^{2+} or Fe^{3+} cation concentration used for clarification.

The results concerning S^{2-} removal showed almost total removal of this parameter. The two iron species (Fe^{2+} and Fe^{3+}) are typically used for sulfide elimination by reaction with sulfide species (Firer et al., 2008). The solubility products of FeS and Fe_2S_3 are $4.9x10^{-18}$ and $1.4x10^{-88}$ (Brown and Holme, 2011).

According to Altaş and Büyükgüngör (2008), ferric ion also reduces the sulfide concentration by being reduced to iron (II), while the sulfide is oxidized to sulfur, Eq. (10), and ferrous ion formed leads to sulfide precipitation. Besides that, S^{2-} is in equilibrium with HS^-, since S^{2-} and HS^- coexist in pH between 9 and 14, with a predominance of S^{2-} when the value is approaching 14 (Shao et al., 2012), and HS^- can react with Fe^{2+}, decreasing S^{2-} concentration, through Eq. (11) (Murugananthan et al., 2004).

$$2\ Fe^{3+} + S^{2-} \rightarrow 2\ Fe^{2+} + S^0 \quad (10)$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (11)$$

According to Firer et al. (2008), ferric ion can also oxidize HS^-, forming Fe^{2+} and S^0, Eq. (12), followed by FeS. In addition, HS^- concentration can decrease by the formation of Fe^{2+} and SO_4^{2-}, Eq. (13), being sulfide concentration reduced due to FeS precipitation.

$$2\ Fe^{3+} + HS^- \rightarrow 2\ Fe^{2+} + S^0 \quad (12)$$

$$8\ Fe^{3+} + HS^- + 4\ H_2O \rightarrow 8\ Fe^{2+} + SO_4^{2-} + 9\ H^+ \quad (13)$$

2.4.2 Electrocoagulation

The electrocoagulation (EC) is a complex process, with a multiplicity of synergetic mechanisms, to remove the pollutants from the wastewater. It comprises the electro dissolution of the sacrificial anode with hydrolysis of metal ions to form hydroxides complexes, the destabilization of the contaminants, and the adsorption of the pollutants in complex hydroxide precipitates to form flakes (Mollah et al., 2004).

There are a wide variety of EC reactor configurations and EC mechanisms in the literature, depending on the different characteristics and compositions of the effluents (Holt et al., 2002). Very often, the electrocoagulation units are used as simple ion supplier and do not take advantage of the electrolytic gases produced in the electrocoagulation process that may promote flotation (Holt et al., 1999). It is a technology used in primary treatment/pretreatment of industrial effluents from agriculture or urban areas (Zongo et al., 2009). The EC with Al and Fe electrodes was patented in the US in 1909. Production of drinking water was the first EC application on a large scale in the US in 1946 (Chen, 2004).

The EC technology has been developed as an alternative for breaking emulsions and stable suspensions in water, using metal salts, polyelectrolytes or polymers (Solak et al., 2009). It has been successfully employed in removing metals, particulate matters, COD, BOD, clay minerals, organic dyes, oil and grease from a variety of industrial effluents (Mollah et al., 2004; Benhadji et al., 2011). Because of the relatively large capital investment and electricity supply costs, electrochemical technology for the treatment of water has not found broad application worldwide (Chen, 2004).

In EC, the coagulant is generated by electrolytic oxidation of a suitable anode material, which produces, at an appropriate pH, the corresponding metal ions that almost immediately hydrolyze to polymeric hydroxides and neutralize the electrostatic charges on the suspended solids surface, enabling the agglomeration or coagulation, and separating them from the aqueous phase (Holt et al., 2002; Kobya et al., 2003; Mollah et al., 2004). The EC mechanism is extremely dependent on the chemistry of the aqueous system, especially its conductivity.

2.4.2.1 Electrocoagulation with aluminum anodes

When direct current passes through aluminum anodes, Al is oxidized to Al^{3+} that dissolves and form metal hydroxide, resulting in colloidal particles, where metal hydroxides are the nucleus (Inan et al., 2004). In the case of Al, metal hydroxide production can occur from two different mechanisms, Eq. (14) to (20) (Ilhan et al., 2008).

Mechanism 1:

Anode (oxidation)

$$Al \rightarrow Al^{3+} + 3\ e^{-} \quad (14)$$

Chemical (in the bulk of the solution/suspension)

$$Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^{+} \quad (15)$$

Cathode (reduction)

$$8\ H^{+} + 8\ e^{-} \rightarrow 4\ H_2 \quad (16)$$

Mechanism 2:

Anode (oxidation)

$$Al \rightarrow Al^{3+} + 3\ e^{-} \quad (17)$$

Chemical (in the bulk of the solution/suspension)

$$Al^{3+} + 3\ OH^{-} \rightarrow Al(OH)_3 \quad (18)$$

Cathode (reduction)

$$2\ H_2O + 2\ e^{-} \rightarrow H_2 + 2\ OH^{-} \quad (19)$$

Overall reaction for the two mechanisms:

$$2\ Al + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2 \quad (20)$$

Simultaneously, according to Mollah et al. (2004), water is also oxidized in the solution's bulk in a parallel reaction, Eq. (21).

$$2\ H_2O \rightarrow 4\ H^{+} + O_2 + 4\ e^{-} \quad (21)$$

The hydrolysis of the aluminum cations can form mononuclear complexes, Eq. (1), (2) and (4). According to Mollah et al. (2004), other species, such as $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, may also be formed over a wide pH range. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles, leading to coagulation. The produced gas, Eq. (19) and (21), can cause flotation of the coagulated material (Mollah et al., 2004; Benhadji et al., 2011). The clusters' coagulation process is identical to that described for CC.

Table 4 lists some conclusions obtained during different treatments of tannery wastewater by electrocoagulation process with the use of aluminum electrodes.

Table 4. Results presented in the literature for tannery wastewaters electrocoagulation with aluminium anodes at different experimental conditions.

Treatment	Parameter	C_0 / mg L^{-1}	Charge / C	$Al^{3+}_{(ad)}$ / mg L^{-1}	pH	Removal / %	Reference
Electro Coagulation	COD	22,500	2157	500.0	3.0	42.0	Şengil et al. (2009)
		7,680	900	83.8	7.5	90.0	Benhadji et al. (2011)
		2,400	3,600	167.8	8.8	50.0	Feng et al. (2007)
		2,995	4,926	91.8	6.8	80.0	Espinoza-Quiñones et al. (2009)
	DOC	1,007	3,600	167.8	8.8	50.0	Feng et al. (2007)
	S^{2-}	2,100	2,157	500.0	3.0	28.0	Şengil et al. (2009)
		110	3,600	167.8	8.8	9.0	Feng et al. (2007)
	NH_3-N	220	3,600	167.8	8.8	68.0	Feng et al. (2007)

C_0= initial concentration of the considered parameter;
$Al^{3+}_{(ad)}$= Al^{3+} cation concentration used for clarification.

Data in Table 4 show different Al^{3+} concentrations applied in the clarification process, which produced different removals rates of the considered parameters. The results not show clear trend of increase or decrease of the efficiency of the clarification by electrocoagulation with aluminum electrode by increasing or decreasing the applied load, which will directly influence the concentration of aluminum cation in the clarification process, i.e., the unique characteristics for each effluent don't allow identify the best $[Al^{3+}]/[COD]$ ratio to maximize COD removal. About the pH influence in the COD removal, the pH values for all authors not show a linear relation with the percentage of COD removal, since it is not clear the tendency of increase or decrease of the COD removal with the variations observed for pH values.

Regarding S^{2-} removal, it is clear the low-yield for this process if it is realized by Al^{3+}, since the S^{2-} removal by aluminum cations tends to be less efficient when compared with the removal by Fe^{3+} cations. This is explained by Eq. (5) and (6) and is related with the solubility product (Ksp) of the possible species formed from S^{2-} with Al^{3+}, Al_2S_3, or with Fe^{3+}, Fe_2S_3. Thus, low S^{2-} removal is expected when aluminum cations are used in the clarification step, since aluminum sulfide is more soluble than iron sulfide.

2.4.2.2 Electrocoagulation with iron anodes

According to Mollah et al. (2001), the EC with consumable iron anode can occur according to two different mechanisms:

Mechanism 1:

Anode (oxidation):

$$4Fe \rightarrow 4\ Fe^{2+} + 8\ e^- \quad (22)$$

$$4\ Fe^{2+} + 10\ H_2O + O_2 \rightarrow 4\ Fe(OH)_3 + 8\ H^+ \quad (23)$$

Cathode (reduction):

$$8\ H^+ + 8\ e^- \rightarrow 4\ H_2 \quad (24)$$

Overall:

$$4\ Fe + 10\ H_2O + O_2 \rightarrow 4\ Fe(OH)_3 + 4\ H_2 \quad (25)$$

Mechanism 2:

Anode (oxidation):

$$Fe \rightarrow Fe^{2+} + 2\ e^- \quad (26)$$

$$Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_2 \quad (27)$$

Cathode (reduction):

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \quad (28)$$

Overall:

$$Fe + 2\ H_2O \rightarrow Fe(OH)_2 + H_2 \quad (29)$$

The Fe^{3+} hydrolysis also leads to the formation of reactive species for wastewater treatment, such as, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_6^{3-}$, $Fe(OH)_4^-$, $Fe(H_2O)_3(OH)_3$, $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, among others, depending on the pH of the system (Mollah et al., 2004; Golder et al., 2005).

Regardless the mechanism, the $Fe(OH)_n$ formed remains in the aqueous phase as a gelatinous suspension, which can remove pollutants from wastewater by complexation or electrostatic attraction, followed by coagulation. In complexation, the pollutant acts as a ligand (L) that binds chemically to the hydrated iron, Eq. (30) (Mollah et al., 2004).

$$L - H + (OH)OFe \rightarrow L - OFe + H_2O \quad (30)$$

Table 5 lists the removal rates of some parameters from tannery wastewater by EC with iron as consumable anode.

Table 5. Results presented in the literature for tannery wastewaters electrocoagulation with iron anodes at different experimental conditions.

Treatment	Parameter	C_0 / mg L^{-1}	Charge / C	$Fe^{n+}_{(ad)}$ / mg L^{-1}	pH	Removal / %	Reference
Electro Coagulation	COD	2,400	3,600	522.4	9.8	54.0	Feng et al., 2007
		22,100	3,960	2,873.0	3.0	80.0	Şengil et al., 2009
		3,700	2,700	1,958.9	9.2	50.0	Apaydin et al., 2009
		5,400	594.1	172.4	8.2	94.0	Kongjao et al., 2008
	DOC	1,007	3,600	522.4	9.8	40.0	Feng et al., 2007
	S^{2-}	110	3,600	522.4	9.8	96.0	Feng et al., 2007
		2,560	3,960	2,873.0	3.0	90.0	Şengil et al., 2009
		440	2,700	1,958.9	9.2	97.0	Apaydin et al., 2009
	$N\text{-}NH_3$	225	3,600	522.4	9.8	31.0	Feng et al., 2007
		180	2,700	1,958.9	9.2	10.0	Apaydin et al., 2009
	TKN	157	594.1	172.4	8.2	62.0	Kongjao et al., 2008

C_0= initial concentration of the considered parameter;
$Fe^{n+}_{(ad)}$= Fe^{2+} or Fe^{3+} cation concentration used for clarification.

Similarly to the discussion for Table 4, the results from literature present at Table 5 show different removals rates for a same parameter, such as COD and $N\text{-}NH_3$, for example. In the same way, the results not show clear trend of increase or decrease for clarification efficiency with the increase of the iron concentration, i.e., the intrinsic characteristics of each effluent do not allow the identification of the best $[Fe^{3+}]/[COD]$ or $[Fe^{3+}]/[N\text{-}NH_3]$ ratio to maximize COD or $N\text{-}NH_3$ removal, respectively. In the same sense, it was noted the influence of the pH in the removal rates of the parameters.

Regarding S^{2-} removal, data made clear the best yield obtained in this process when iron cations are used. As can seem at Table 5, the minimum removal was 90% for Şengil et al., 2009. This is aligned with the high efficiency of S^{2-} removal by iron cation, since the iron sulfides formed through reaction between S^{2-} and Fe^{2+} or Fe^{3+}, present low solubility, increasing the sulfide removal by sedimentation. Anyway, the results concerning S^{2-} removal showed an almost total removal, i.e., EC seems to be an efficient way for S^{2-} removal.

2.4.3 Chemical Coagulation *vs*. Electrocoagulation for organic load removal

The literature results regarding COD abatement by CC or EC, with aluminum or iron cations, are presented in Tables 2 to 5. In order to find the best performance for COD abatement between these different technologies, data from those tables was compared. Figure 1, a and b, present, respectively, plots of COD removal vs. $[X^{3+}_{(ad)}]/COD_0$ and $(COD_0 - COD_{final})$ vs. COD_0, where $X^{3+}_{(ad)}$ stands for aluminum or iron cations added, in mg L^{-1}. It can be observed (Figure 1a) that the best results for all the tested techniques were obtained for $[X^{3+}_{(ad)}]/COD_0$ lower than 0.1, meaning that probably there is no need for adding high quantities of aluminum or

iron ions, since, according to already referred, these ions are regenerated during the coagulation process. This conclusion is corroborated by data presented in Figure 1b, which shows a linear relation between COD removed and initial COD, i.e., the higher the initial COD the higher the COD removed.

Regarding the efficiency of the different operations, it is not possible to assume, without any doubt, which one is the best process for COD removal, although EC with Fe seems to lead to the poorest results.

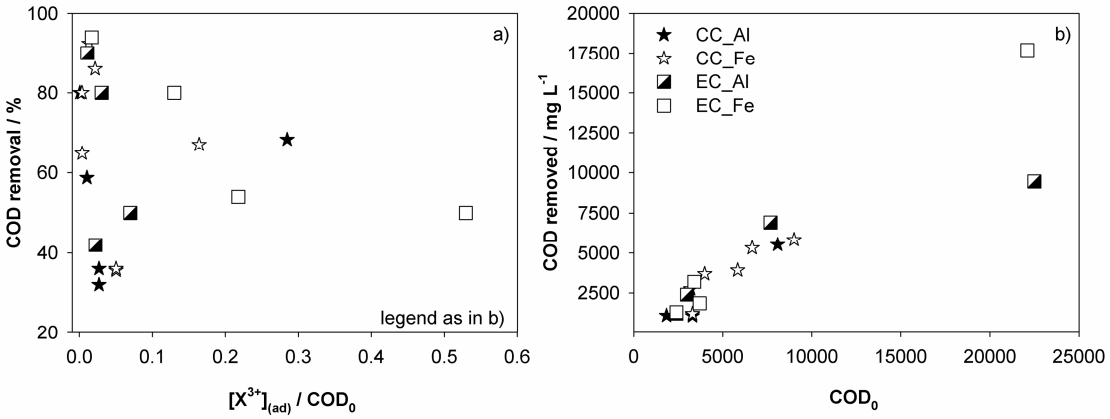

Figure 1. Variation of (a) COD removal with $[X^{3+}_{(ad)}]/COD_0$ and (b) (COD_0 – COD_{final}) with COD_0 for data presented in the literature (see Table 3 to 6) for different techniques utilized in COD abatement. $X^{3+}_{(ad)}$: aluminum or iron cations added.

2.5 Anodic oxidation, a new horizon

2.5.1 General characteristics

As already pointed out, effluents from tanning industry vary greatly, and present low biodegradability, being a serious environmental and technological problem (Di Iaconi et al., 2002). Conventional technologies, which include biological processes followed by sedimentation, filtration, among others, may present poor reliability, economically infeasible and low efficiency and are not enough to reach the level of purification needed to eliminate the negative impact on the environment (Panizza et al., 2008; Naumczyk and Kucharska, 2011).

The presence of recalcitrant pollutants to conventional biological and chemical treatments, along with the strict restrictions imposed by legislations have encouraged the search for alternatives to the existing conventional treatments. In recent years many scientific works have been focused on advanced oxidation processes, like photochemical oxidation, ozonation, Fenton oxidation and electrochemical oxidation, which offer effective wastewater purification performance and can eliminate persistent pollutants (Woisetschläger et al., 2013).

The application of emerging technologies have been studied either as an alternative to the conventional treatments or as a complement in tannery wastewaters treatment (Schrank et al., 2004). Among these emerging technologies, electrochemical processes received great attention, since they present high treatment efficiencies (Feng et al., 2003). These processes offer: (a) flexibility, (b) automation, and (c) environmental compatibility (Costa et al., 2008).

Electrochemical reactors have been used since the early 1960's in pollutants recovering from electroplating industry, and were recently considered for other applications, since they can either lead to the total mineralization of the organic pollutants or to the formation of intermediate species, resulting in an enhancement of the biodegradability of the effluent (Szpyrkowicz et al., 2001). According to Kurt et al. (2007), the kinetics of the electrochemical processes is about 100 times faster than biological oxidation processes.

The electro-oxidation of wastewater containing toxic pollutants has been applied successfully to the treatment of different types of wastewaters. In the case of the tannery wastewaters, which have good conductivity and a high chloride concentration, electrochemical methods may be effective as a final polishing step because the pollutants can be oxidized by direct and indirect process (Apaydin et al., 2009).

It has been reported that the presence of high concentrations of ions, especially chlorides, favors the electro-oxidation process, which makes tannery wastewaters suitable for the application of this treatment (Szpyrkowicz et al., 2001). Panizza and Cerisola (2004) reported that, for tannery wastewaters, which present good conductivity and high chloride ions concentration, electrochemical methods have shown to be effective as a polishing step, where organic pollutants, NH_4^+ and S^{2-}, were oxidized by direct and indirect oxidation through electrogenerated Cl_2.

According to Panizza et al. (2010), the oxidation of contaminant organic matter (R), can occurs by direct, Eq. (31), or indirect oxidation, Eq. (32) to (34), through the electrogeneration of strong oxidizing agents, like Cl_2, on the surface of the anode, which subsequently destroy the pollutants in the solution.

$$R + H_2O \rightarrow CO_2 + H^+ + e^- \quad (31)$$

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \quad (32)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (33)$$

$$R + HOCl \rightarrow CO_2 + H_2O + HCl \quad (34)$$

Although the oxidation of the organic matter can be attributed to two different processes, direct and indirect oxidation, the effective degradation of contaminants is based on the direct electrochemical process and depends mainly on the reaction with $^{\bullet}OH$ radicals on the

electrode's surface (Vlyssides and Israilides, 1997). The •OH radical has a high standard reduction potential (E = 2.80 V vs SHE) that makes it capable of non-selectively reaction with organic molecules until their complete mineralization to CO_2, water and inorganic ions (Brillas et al., 2007).

In addition to the organic load removal, the electrochemical oxidation process has been shown as a promising alternative for ammonium removal from different types of wastewaters by indirect oxidation, and the reaction with ammonium is of primary importance (Szpyrkowicz et al., 1995). Ammonium degradation takes place by chlorine generation, Eq. (32), followed by HClO formation, Eq. (33). Finally, the HClO oxidizes the NH_4^+, Eq. (35) (Cabeza et al., 2007):

$$2\ NH_4^+ + 2\ HClO \rightarrow N_2 + 2\ H_2O + 6\ H^+ + 2\ Cl^- + 2\ e^- \qquad (35)$$

Anodic oxidation can be very effective in removing contaminants from effluents, but unwanted chemical species can be formed during the process. In fact, Costa et al. (2008) verified the formation of Cr(VI) from Cr(III) in anodic oxidation of tannery effluent using DSA electrodes.

According to Apaydin et al. (2009), electrochemical oxidation effectiveness depends strongly on the nature of the electrode material, and there are several studies focused on pollutants oxidation efficiency with different electrodes, improvement of the electrocatalytic activity and electrochemical stability of the electrode materials, factors that affect the process performance, the mechanisms and kinetics of the pollutants degradation, among others (Chen (2004).

According to Panizza et al. (2008), although several anode materials have been tested for the electrochemical oxidation of organic compounds, the complete mineralization to CO_2 and good energetic efficiency was obtained only using high oxygen overpotential anodes, such as SnO_2, PbO_2 and BDD.

2.5.2 The influence of the electrode material

Although there are several different materials that can be used as anode in the degradation of organic pollutants, this subchapter will be only focused on the performances of lead oxide, antimony and stannous mixed oxides and boron-doped diamond as anode materials.

2.5.2.1 Metal oxides

Metal oxide anodes have attracted the attention of researchers due to their high conductivity and oxidation capability (Feng et al., 2003). Several metal oxides were already tested as

anodes in the electrodegradation of wastewaters, being lead oxide and antimony and stannous mixed oxides among those most widely investigated. In fact, Ti/SnO_2 and Ti/PbO_2 anodes have shown effectiveness in the removal of several organic pollutants from different wastewaters, in addition to demonstrating effectiveness in the removal of $N\text{-}NH_4^+$ (Chiang et al., 1995; Rao et al., 2001; Chiang et al., 2001; Szpyrkowicz et al., 2005).

The indirect oxidation of organic matter, R, at the oxide anodes (MO_x) surface starts with water electrolysis, producing adsorbed $^{\bullet}OH$ radicals, Eq. (36), with subsequent oxidation of R, Eq. (37). The $^{\bullet}OH$ adsorbed radicals can form adsorbed oxygen, chemically active, Eq. (38), which can promote the oxidation of R, Eq. (39); other strong oxidants, Cl_2 and HOCl, can be produced in many effluents containing chlorides through Eq. (32) and (33), respectively (Comninellis, 1994).

$$H_2O + MO_x \rightarrow MO_x[^{\bullet}OH] + H^+ + e^- \quad (36)$$

$$R + MO_x[^{\bullet}OH] \rightarrow MO_x + CO_2 + z\,H^+ + z\,e^- \quad (37)$$

$$MO_x[^{\bullet}OH] \rightarrow MO_{x+1} + H^+ + e^- \quad (38)$$

$$MO_{x+1} + R \rightarrow MO_x + RO \quad (39)$$

Other strong oxidants can be produced from the generated HOCl, such as OCl^-, Eq. (40), which can contribute to the elimination of the contaminant [Anglada et al. (2009)].

$$HOCl \rightarrow H^+ + OCl^- \quad (40)$$

The results reported by Ciríaco et al. (2009) showed that the $Ti/Pt/PbO_2$ anode presented considerable efficiency in total organic carbon and COD removals. Panizza and Cerisola (2004) also obtained good results in COD reduction during the electro-oxidation of simulated effluent, containing tannic acid, with Ti/PbO_2 anodes.

Santos et al. (2013) applied $Ti/SnO_2\text{–}Sb_2O_4$ and $Ti/Pt/SnO_2\text{–}Sb_2O_4$ electrodes in the anodic oxidation of pharmaceutical drugs, having achieved very good COD and DOC removals particularly with $Ti/SnO_2\text{–}Sb_2O_4$ anode. However, electrode's lifetime is deeply increased when the Pt interlayer is introduced. Authors have noticed the great influence on the degradation results of the electrode preparation method and the applied current density.

The versatility of metal oxide anodes was also described by Rao et al. (2001), which reduced the COD and $N\text{-}NH_4^+$ levels, present in tannery effluent samples, using Ti/PbO_2 and Ti/MnO_2 anodes. Using Ti/PbO_2, the COD removals were between 64.2 and 71.3%, for an initial COD of 533.3 mg L^{-1}, and the $N\text{-}NH_4^+$ removals varied between 48.1 and 78.4 %, for an initial $N\text{-}NH_4^+$ of

103.7 mg L^{-1}. Panizza and Martinez-Huitle (2013) reported COD and N-NH_4^+ removals of 70 and 95%, respectively, after 4 hours of electrolysis of a landfill leachate, with initial COD and N-NH_4^+ of 780 and 266 mg L^{-1}, respectively. Similar results were achieved by Panizza et al. (2010).

Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 anodes were tested in samples with high organic load (initial COD of 6,200 mg L^{-1}) by Fernandes et al. (2014), and the results showed COD removals of 37 and 40% for Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4, respectively, after 8 h of treatment at a current density of 30 mA cm^{-2}. Regarding N-NH_4^+ removals, 90 and 65% were achieved for Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 anodes, respectively, for an initial N-NH_4^+ concentration of 480 mg L^{-1}. These authors reported high removal rates of ammonium nitrogen and total nitrogen (TN).

In the last two decades, the literature provided several studies about anodic oxidation using SnO_2 anode. However, in these works, such as Comninellis and Pulgarin (1991), Comninellis and Pulgarin (1993), Comninellis and Nerini (1995), Polcaro et al. (1999), Zanta et al. (2003), Chen et al. (2005) and Waterston et al. (2006), among others, the process is focused on the oxidation of phenol and its derivatives. For real effluent, papers are very scarce and only few studies, such as Fernandes et al. (2014), are found.

According to Li et al. (2013) metal oxides electrodes have several advantages, like low cost, long life-time, great stability, high availability, and strong electrocatalytic activity for chlorine evolution, which can improve indirect oxidation of recalcitrant organic compounds. Since PbO_2 electrode meets all these requirements and is effective in oxidizing pollutants, it becomes the most widely investigated metal oxide anode material for electro-oxidation (Chen, 2004).

Although there are a lot of works about electro-oxidation of various pollutants, the application of anodic oxidation to tannery wastewater is still relatively scarce, and there are only a few electrode materials that have already been tested. Table 6 contains some results reported in the literature.

2.5.2.2 Boron-doped diamond - BDD

Boron-doped diamond electrodes have been described as presenting high organic oxidation levels (Anglada et al., 2009). This anode material is known for its high chemical stability, its inert surface and long lifetime (Cabeza et al., 2007). However, a BDD anode is still very expensive, and thus the industrial applications are currently very limited (Chen et al., 2003).

BDD anodes also present a high overpotential for O_2 evolution, much higher than that of conventional anodes, producing large amounts of weakly adsorbed $^{\bullet}OH$, Eq. (41), and thereby resulting in a rapid and effective pollutants degradation (Palma-Goyes et al., 2010).

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \quad (41)$$

Thus, an organic pollutant, R, may be oxidized by the BDD($^{\bullet}$OH) formed, Eq. (42) (Fóti et al., 1999). At same time, oxygen can be generated from the adsorbed $^{\bullet}$OH, equation (43) (Chen et al., 2003).

$$R + BDD(^{\bullet}OH) \rightarrow BDD + CO_2 + z\,H^+ + z\,e^- \quad (42)$$

$$BDD(^{\bullet}OH) \rightarrow BDD + \tfrac{1}{2}\,O_2 + H^+ + e^- \quad (43)$$

According to Palma-Goyes et al. (2010), the BDD high oxidizing power allows simultaneous formation of several side-oxidants, such as H_2O_2, $S_2O_8^{2-}$ and O_3, through Eq. (44) to (46), respectively, as well as chlorinated oxidants.

$$2\,BDD(^{\bullet}OH) \rightarrow 2\,BDD + H_2O_2 \quad (44)$$

$$2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,e^- \quad (45)$$

$$3\,H_2O \rightarrow O_3 + 6\,H^+ + 6\,e^- \quad (46)$$

The onset potential for O_2 evolution on BDD is higher than that on PbO_2 and SnO_2, for example, and indicates that BDD electrodes have higher current efficiency for pollutant oxidation (Chen, 2004).

The literature about the oxidation of real tanning effluents using BDD anodes is still scarce and only one study was found in the literature (Isarain-Chávez et al., 2014). However, several works have demonstrated the effectiveness of BDD electrode in pollutants removal, in the form of organic load, nitrogen-containing compounds, like ammonia, among others (Kraft, 2007; Anglada et al., 2009; Panizza and Cerisola, 2009; Sirés and Brillas, 2012; Ganzenko et al., 2014; Sirés et al., 2014).

Table 6. Results presented in the literature for tannery wastewaters electro-oxidation at different experimental conditions.

Parameter initial concentration / mg L^{-1}		Current density / mA cm^{-2}	Samples volume / mL	Time / h	Electrode material (area/cm^2)	Removal / %	Reference
COD	544.0	16.7	200	4	Ti/PbO_2 (30)	71.3	Rao et al., 2001
	515.0	55.6	60		Ti/Pt (9)	62.0	
	8540.0	261.1	15000	3	Ti/Pt (383)	84.0	Vlyssides and Israilides, 1997
	1774.0	30	640	1.0	Ti/Pt (100)	46.4	Szpyrkowicz et al., 1995
		30		0.5	Ti/Pt/Ir (100)	10.9	
TOC	1005.0	50	50	5	$Ti/Ru_{0.30}Ti_{0.70}O_2$ (1)	31.3	Isarain-Chávez et al., 2014
	1875.0	65	250	3	BDD (7.6)	48.0	Costa et al., 2008
NH_4^+	102.0	16.7	200	4	Ti/PbO_2 (30)	78.4	Rao et al., 2001
	107.0	55.6	60		Ti/Pt (9)	96.0	
	125.0	30	640	1	Ti/Pt (100)	79.2	Szpyrkowicz et al., 1995
		30		0.5	Ti/Pt/Ir (100)	99.2	
S^{2-}	385.0	261.1	15000	3	Ti/Pt (383)	~100	Vlyssides and Israilides, 1997
	1.99	16.7	200	4	Ti/PbO_2 (30)	64.8	Rao et al., 2001
	2.0	55.6	60		Ti/Pt (9)	88.0	
	352.0	40	1000	0.38	Ti/Pt/Ir (100)	99.4	Szpyrkowicz et al., 2005
	232.0			0.37	$Ti/PbO\text{-}Co_3O_4$ (100)	99.1	

3 ANALYTICAL METHODS FOR PARAMETERS DETERMINATION

This chapter describes the analytical methods utilized for the determination of the different parameters used to follow contaminants removal during the proposed treatments. It also presents the specifications of the equipment utilized to perform the analytical determinations.

3.1 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) often is used as a measurement of pollutants in wastewater and natural waters. It is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion is the specified oxidant for this method. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest (APHA, 2005)

The COD analysis was performed according to APHA (2005), section 5220 C. For this, the sample was refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed. The oxidizable matter was calculated in terms of oxygen equivalent.

3.2 Total Dissolved Carbon, Total Dissolved Organic and Inorganic Carbon

The carbon in water and wastewater is composed of a variety of compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes. These fractions of carbon are defined as: inorganic carbon, total organic carbon; dissolved organic carbon, suspended organic carbon, among others.

The Total Dissolved Carbon (TDC) represents all the carbon in the sample, including both inorganic and organic carbon, and Dissolved Organic Carbon (DOC) and Dissolved Inorganic Carbon (DIC) are the fractions of organic and inorganic carbon, respectively, that pass through a 0.45 μm pore-diameter filter.

In the present study, Total Dissolved Carbon, Dissolved Inorganic Carbon and Dissolved Organic Carbon were measured by a Shimadzu TOC-CPH analyzer combined with a TNM-1 unit,

which combines a combustion catalytic oxidation at 680°C and a non-dispersive infrared detection methods.

For TDC determinations, an automated process injected the sample into the combustion furnace, where it undergoes combustion through heating at 680 ºC, with a platinum catalyst in an oxygen rich atmosphere. The water is vaporized and the organic and inorganic carbons are oxidized to CO_2 and H_2O. The gas phase, containing the CO_2, is transported in the carrier gas through a moisture trap and halide scrubbers, to remove water vapour and halides from the gas stream before it reaches the detector. The CO_2 generated concentration is then measured with non-dispersive infrared detector. DIC is measured separately by injecting the sample into a reaction chamber where it is acidified, and all inorganic carbon is converted to CO_2, which is carried to the detector and measured. The DOC value is determined by the difference between TDC and TIC.

In this method, samples are homogenized, and diluted as necessary, and injected into a heated reaction chamber packed with an oxidative catalyst. The water is vaporized and the organic carbon is oxidized to CO_2. The CO_2 from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a nondispersive infrared analyzer. Because total carbon is measured, inorganic carbon must be removed by acidification and sparging or measured separately and DOC obtained by difference.

3.3 Nitrogen: Kjeldahl, Ammonia and Total

The element Nitrogen is a primary growth ingredient found in numerous chemical compounds. In waters and wastewaters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as Kjeldahl Nitrogen. Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen, ammonia (NH_3), and ammonium (NH_4^+). Environmentally, the term ammonia refers to two chemical species which are in equilibrium in water (NH_3, un-ionized and NH_4^+, ionized). Total Nitrogen (TN) is the sum of nitrate-nitrogen ($N\text{-}NO_3^-$), nitrite-nitrogen ($N\text{-}NO_2^-$), ammonia-nitrogen ($N\text{-}NH_3$), ammonium-nitrogen ($N\text{-}NH_4^+$) and organically bonded nitrogen.

TKN was determined using a Kjeldatherm block digestion system and a Vapodest 20 s distillation system, both from Gerhardt, and an automatic titrator Metrohm 876 Dosimat Plus.s, according to APHA (2005) section 4500-N_{org} B. According to this section, in the presence of sulfuric acid, potassium sulfate, and cupric sulfate catalyst, amino nitrogen of many organic materials is converted to ammonium. Free ammonia is also converted to

ammonium. After addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia is determined by titration with a standard mineral acid.

The concentration of ammonia nitrogen was determined in the distillation Vapodest Gerhardt 20s, according to APHA (2005) sections 4500-NH_3 B and C. For this, the sample is buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds. Then, it is distilled into a solution of boric acid and the ammonia in the distillate is determined titrimetrically with standard H_2SO_4 and a mixed indicator.

TN was measured in a Shimadzu TNM-1 unit coupled with the TOC-VCPH analyser. All nitrogen present in samples is first converted to nitrogen monoxide and nitrogen dioxide by catalytic combustion in the furnace. The nitrogen species are then reacted with ozone, to form an excited state of nitrogen dioxide. Upon returning to ground state, the emitted light energy is measured, using a chemiluminescence detector, and converted to TN.

3.4 Sulfate, Nitrate, Nitrite, Chloride, Sulfide, Sulfur and Ammonium

The concentrations of SO_4^{2-}, NO_3^-, NO_2^-, Cl^- and NH_4^+ were determined by ion chromatography, using a Shimadzu 10AVP HPLC instrument coupled with a conductivity detector Shimadzu CDD 10AVP. The determinations of anions was performed using an IC I-524A Shodex (4.6 mm ID×100 mm) anion column at 40 ◦C and an aqueous solution of 2.5 mM of phthalic acid and 2.3 mM of tris(hydroxymethyl)aminomethane as a mobile phase at a flow rate of 1.5 mL min^{-1}. Before each HPLC run, the samples were filtered on Whatman filter with porosity 0.2 μm.

For NH_4^+ determination, an IC YK-A Shodex (4.6 mm ID × 100 mm) column at 40 ºC was used. The isocratic elution mode was used and the mobile phase was a 5.0 mM tartaric acid, 1.0 mM dipicolinic acid and 24 mM boric acid aqueous solution at a flow rate of 1.0 mL min^{-1}.

The presence of sulfur on the electrode surface was investigated by SEM/EDS/X-ray (Scanning Electron Microscopy (SEM), Dispersive Energy Spectroscopy (EDS) performed in a Hitachi (S-2700)/Oxford (60–74) system operating at 20 keV, and X-ray powder diffraction (XRD) Rigaku DMAXIII/C).

The determination of S^{2-} concentration was performed according to APHA (2005), section 4500-S^{2-} F. In this method, sulfide reacts with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate, using starch as an indicator.

3.5 Total Chromium, Chromium(VI), Aluminum and Iron

Total chromium, iron and aluminum concentrations were performed by Flame Atomic Absorption Spectroscopy (Perkin Elmer AAnalyst 800) according to APHA (2005) section 3111 B for iron and chromium, for aluminum, section 3111 D.

In flame atomic absorption spectroscopy, a sample previously digested by HNO_3-HCl in a reflux system is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame, and a calibration curve is used to determine the unknown concentration of an element in a solution.

The Cr(VI) concentration was realized according to APHA (2005) section 3500-Cr B using a Shimadzu UV-Vis Spectrophotometer UV-1800. In this technique, the hexavalent chromium, Cr(VI), is determined colorimetrically by reaction with diphenylcarbazide in acid solution that produces a red-violet colored complex of unknown composition. From a calibration curve which contains Cr(VI) concentration *vs*. Absorbance, and the absorbance determined by the Spectrophotometer, the unknown Cr(VI) concentration is determined.

3.6 pH, Conductivity, Electric Potential and Turbidity

Acidity of a water is its quantitative capacity to react with a strong base to a selected pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulfates may contribute to the measured acidity according to the method of determination. The measurement also reflects a change in the quality of the source water.

Conductivity is a measure of the ability of an aqueous solution to carry an electric current which interferes in the Electric Potential. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic species are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

The clarity of a natural body of water is an important determinant of its condition and productivity. Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample. Correlation of turbidity with the weight or particle number concentration of

suspended matter is difficult because the size, shape, and refractive index of the particles affect the light-scattering properties of the suspension.

In this work, the pH was measured using a Hanna pH meter (HI931400) and the conductivity with a Mettler Toledo conductivity meter (SevenEasy S30K). The potential was verified on the own power supply (Laboratory DC Power Supply, Model GPS-3030D; 0-30 V, 0-3 A) used in the assays. The CC and EC assays were performed in the Jar Test Lovibond Floc-Tester ET 730. The turbidity was verified in the digital turbidimeter Orbeco-Hellige 965-10.

4 RESULTS AND DISCUSSIONS

This chapter starts with the results obtained regarding the effect of the current density in the kinetic of the conversion S^{2-} to SO_4^{2-}, section 4.1. Following the latter, are presented the performances of metal oxide and BDD electrodes to remove contaminants in tannery effluents, section 4.2. In sections 4.3 and 4.4 are evaluated the performances of two clarifying agents, aluminum and iron, used on the pretreatment of tannery wastewater in order to study their effects on the contaminant removal by anodic oxidation. In the last section, 4.5, are discussed the results obtained for the efficiency of contaminant removal by anodic oxidation in recirculation system of a pretreated effluent by iron.

4.1 Sulfide oxidation with BDD: Effect of the current density on the kinetic of the conversion to sulfate

The objective of this study was to evaluate the effect of the current density on the kinetics of the conversion of sulfide into sulfate, by anodic oxidation at a BDD electrode, using high sulfide concentration.

A boron doped diamond anode, BDD, purchased from Adamant Technologies (now NeoCoat), with an area of 10 cm^2, and a stainless steel plate cathode, with similar area, were used. Current densities were imposed by a power supply unit, Laboratory DC Power Supply, Model GPS-3030D (0-30 V, 0-3 A). Stirring (100 rpm) was accomplished by a magnetic stirrer, Metrohm AG.

Na_2S solutions, 500 mL, with S^{2-} concentration of 1,953.03 ± 48.70 mg L^{-1} (approximately 60 mM) were electrolyzed in an open system, during the proposed experimental periods, with removal of 20 mL sample each hour for the respective analyzes: 10 mL for the determination of S^{2-} concentration, 5 mL to pH and conductivity measurements and 5 mL for the determination of SO_4^{2-} concentration. The presence of sulfur on the surface of BDD was investigated by SEM/EDS/X-ray.

The current density (mA cm^{-2}) and the run time (h) applied, (mA cm^{-2}/h) were 10/42, 20/20, 30/20, 40/20, 50/17 and 60/15.

4.1.1 Sulfur and polysulfides: production and features

In all the sulfide electro-oxidation assays, it was observed the formation of a yellow deposit on the surface of the BDD anode (Figure 2a). Figure 2b presents a SEM micrograph of the yellow powder, with a magnification of 4000 times, that was confirmed as sulfur by X-ray powder diffraction (data not shown) and EDS analyses (Figure 2c).

The extent of the formation of the sulfur deposit was directly associated to the current intensities used, i.e., the formation of sulfur on the surface of the anode increased with the increase of the applied current density from 10 to 60 mA cm^{-2}. This characterizes the occurrence of reaction with sulfur formation, Eq. (47) (Awe et al., 2013). Similar results were also obtained by other authors (Ateya and Al-Kharafi, 2002; Ateya et al., 2005; Waterston et al., 2007; Haner et al., 2009; Al Kharafi et al., 2010; Hastie et al., 2011; Pikaar et al., 2011a; Awe et al., 2013).

$$S^{2-} \rightarrow S + 2\,e^{-} \qquad E^{o} = -476\ mV \qquad (47)$$

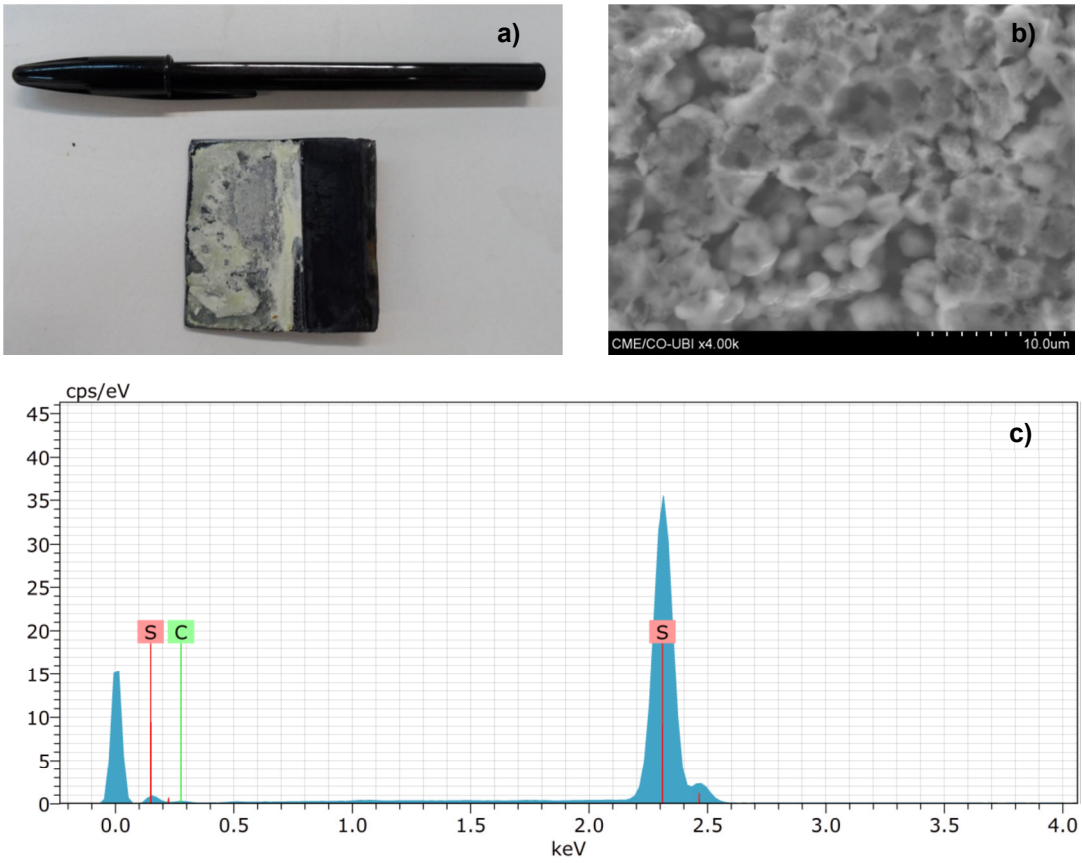

Figure 2. a) Photograph and b) micrograph, with a magnification of 4000x, of the sulfur formation on BDD surface, and results from the c) EDS analysis..

During the assays performed at 10, 20 and 30 mA cm^{-2} no significant variation of the potential was observed, whereas for the assays performed at 40, 50 and 60 mA cm^{-2} applied current densities it decreased in the begin of the assays and increased after some time, as can be seen in Figure 3a. For higher current densities, the initial decrease must be related to an increased in the formation rate of sulfate rather than sulfur that would also be responsible for a partial polarization of the electrode's surface.

The polarization by sulfur formation may explain the initial slight increase in potential at 20 and 30 mA cm^{-2}, since at low current densities reactions involving less electrons transfer, Eq. (47) (Awe et al., 2013), become more important. In their works, Ateya and Al-Kharafi (2002), Ateya et al. (2005) and Dutta et al. (2008) found that the formation of sulfur promoted the passivation of the electrode. This seemed to be derived from the porosity of graphite electrode that caused a strong adhesion to the electrode's surface of the sulfur formed, leading to greater difficulty in the transfer of the electric charge.

The sulfur deposition on the electrode surface, with subsequent passivation, was also observed by Miller and Chen (2005) with a Ti/Ta_2O_5-IrO_2 electrode. This situation seems to be due to the possibility of strong adsorption of the sulfur formed on the electrode surface because, typically, the metal oxide electrodes have higher roughness than the BDD. These results were substantially different from those obtained by Pikaar et al. (2011b), since they have not observed the presence of elemental sulfur on the surfaces of electrodes. This situation appears to be associated with the low current density used by the authors, 10 mA cm^{-2}, and the low S^{2-}concentration, 10 mg L^{-1}.

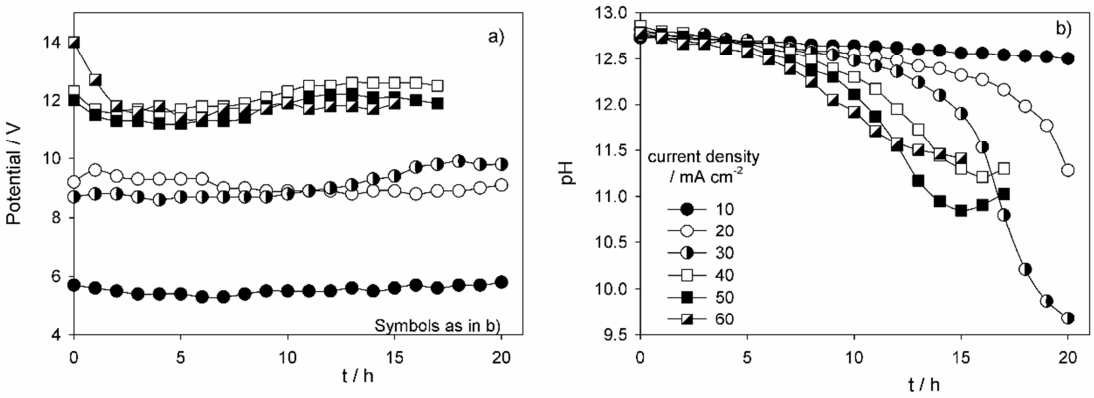

Figure 3. Variation in time of the a) potential difference between anode and cathode and b) pH for the assays performed at different applied current densities: $[S^{2-}]_0$ = 60 mM.

Besides the formation of sulfur on the anode's surface, it was also observed the development of a yellow color. According to the literature (Kleinjan et al., 2005; Waterston et al., 2007; Haner et al., 2009; Hastie et al., 2011), this phenomenon was related with the formation of polysulfides, S_x^{2-} (where x= 2, 3, 4, ….). The sulfur formed can react with S^{2-} forming S_2^{2-}, Eq. (48), which can be oxidized, Eq. (49) to (51), providing the intensification of the color (Ateya et al.,2005). The S_2^{2-} may also be formed via Eq. (52) (Valensi et al., 1963). The fact that the elemental sulfur concentration remains stable for most of the time indicates that the rates of reactions described in Eq. (48), (55) to (58) (Awe et al., 2013), and (61) (Ateya and Al – Kharafi, 2002), are smaller than the formation rate of the elemental sulfur, Eq. (47) and (54)(Awe et al., 2013), under the experimental conditions of this work.

$S^{2-} + S \rightarrow S_2^{2-}$ (48)

$3\ S_2^{2-} \rightarrow 2\ S_3^{2-} + 2\ e^-$ E^o= -506 mV (49)

$4\ S_3^{2-} \rightarrow 3\ S_4^{2-} + 2\ e^-$ E^o= -478 mV (50)

$5\ S_4^{2-} \rightarrow 4\ S_5^{2-} + 2\ e^-$ E^o= -441 mV (51)

$2\ S^{2-} \rightarrow S_2^{2-} + 2\ e^-$ E^o= -524 mV (52)

$2\ S + 3\ H_2O \rightarrow S_2O_3^{2-} + 6\ H^+ + 4\ e^-$ E^o= 0.165 mV (53)

$S_2^{2-} \rightarrow 2\ S + 2\ e^-$ E^o= -0.310 mV (54)

$4\ S + 12\ OH^- \rightarrow S_4O_6^{2-} + 6\ H_2O + 10\ e^-$ E^o= -578 mV (55)

$S + 6\ OH^- \rightarrow SO_3^{2-} + 3\ H_2O + 4\ e^-$ E^o= -657 mV (56)

$2\ S + 6\ OH^- \rightarrow S_2O_3^{2-} + 3\ H_2O + 4\ e^-$ E^o= -743 mV (57)

$S + 8\ OH^- \rightarrow SO_4^{2-} + 4\ H_2O + 6\ e^-$ E^o= -747 mV (58)

$2\ S + 3\ H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4\ e^-$ E^o= 0.165 mV (59)

The hydrolysis of S^{2-} occurs in two steps, according to the following equilibrium, Eq. (60) and (61) (Rysselberghe and Gropp, 1944):

$S^{2-} + H_2O \rightarrow HS^- + OH^-$ K_1= 10 (60)

$HS^- + H_2O \rightarrow H_2S + OH^-$ K_2= 10^{-7} (61)

The values for the equilibrium constants K_1 and K_2 indicate that reaction (61) occurs in a much smaller extent than (60). Thus, the characteristics of the solution from the S^{2-} hydrolysis, high pH and the presence of HS^-, will be determined by reaction (60). In fact, all the initial solutions presented pH above 7, ranging between 12.7 and 12.9. It was noted that pH was reduced during the experiment, as can be seen in Figure 3b. The results showed that the intensity of pH reduction appeared to be directly related to the applied current density, particularly during the first 10 hours of the experiments. The decrease in pH is associated with the occurrence of reactions presented in Eq. (55) to (58), among others, since the S^{2-} consumption is followed by OH^- consumption. The reactions depicted in Eq. (62) to (64) (Awe et al., 2013), related to the oxidation of intermediate species ($S_2O_3^{2-}$, $S_4O_6^{2-}$ and SO_3^{2-}), eventually produced, show also the consumption of OH^-, which decreases the pH.

$S_2O_3^{2-} + 10\ OH^- \rightarrow 2\ SO_4^{2-} + 5\ H_2O + 8\ e^-$ $E^o = -799$ mV (62)

$S_4O_6^{2-} + 20\ OH^- \rightarrow 4\ SO_4^{2-} + 10\ H_2O + 14\ e^-$ $E^o = -872$ mV (63)

$SO_3^{2-} + 2\ OH^- \rightarrow SO_4^{2-} + H_2O + 2\ e^-$ $E^o = -920$ mV (64)

Another interesting situation is associated with Eq. (65) to (67) (Valensi et al., 1963), because their occurrence reduces S^{2-} concentration, inducing the displacement of Eq. (60), to produce S^{2-} with OH^-consumption, intensifying the decrease in pH. After 15 h of the assay run at 50 mA cm^{-2}, and 16 h for 40 mA cm^{-2}, i.e., when the removal of S^{2-} was already very high, it was noted a subtle increase of the pH, Figure 3b. This situation may be derived from the occurrence of Eq. (68) and (69) (Milazzo et al., 1978), due to the presence of intermediate species generated during the process. This fact would also explain lower decrease in pH after 10 hours run for the assay performed at an applied current density of 60 mA cm^{-2}.

$2\ S^{2-} + 3\ H_2O \rightarrow S_2O_3^{2-} + 6\ H^+ + 8\ e^-$ $E^o = -6$ mV (65)

$S^{2-} + 3\ H_2O \rightarrow SO_3^{2-} + 6\ H^+ + 6\ e^-$ $E^o = 231$ mV (66)

$S^{2-} + 4\ H_2O \rightarrow SO_4^{2-} + 8\ H^+ + 8\ e^-$ $E^o = 149$ mV (67)

$2\ SO_3^{2-} + 3\ H_2O + 4\ e^- \rightarrow S_2O_3^{2-} + 6\ OH^-$ $E^o = -571$ mV (68)

$2\ SO_3^{2-} + 2\ H_2O + 2\ e^- \rightarrow S_2O_4^{2-} + 4\ OH^-$ $E^o = -1120$ mV (69)

4.1.2 Sulfide removal: effect of current density and kinetic aspects

About sulfide removal, the results showed that it is strongly influenced by the current density, Figure 4a. Similar results were also found by other authors (Waterston et al., 2007; Haner et al., 2009; Hastie et al., 2011; Pikaar et al., 2011b).

The efficiency of the electro-oxidation process, expressed as sulfide removal versus electrical charge passed, at the different applied current densities, is depicted in Figure 4b, showing a decrease in efficiency with the increase in applied current due to an increase in the relevance of the diffusional step. After 8 h of electrolysis, sulfide removals were 34.3, 84.8, 97.8, 99.8, 99.2 and 99.4% for the applied current densities of 10, 20, 30, 40, 50 and 60 mA cm^{-2}, respectively.

Further analysis showed that, if it is considered the time needed to remove 50% of the initial [S^{2-}] (inset of Figure 4b), the increasing current density does not decrease substantially the time needed to achieve the desired removal, particularly for current densities between 40 and 60 mA cm^{-2}, since for these current densities the time decreases from 6.2 to 4.9 h. Nevertheless, when the density increases from 10 to 40 mA cm^{-2}, the time to achieve 50% removal in [S^{2-}] is reduced from 29.8 to 6.2 h. The influence of the current density on the S^{2-}

consumption is shown by the occurrence of the reactions (47) and (70) to (73) (Awe et al., 2013); (54) and (65) to (67) (Valensi et al., 1963), since the increase in current density tends to enhance the occurrence of those reactions, having also influence on their relative occurrence.

$$4\ S^{2-} + 12\ OH^- \rightarrow S_4O_6^{2-} + 6\ H_2O + 18\ e^- \qquad E^o = -542\ mV \qquad (70)$$

$$S^{2-} + 6\ OH^- \rightarrow SO_3^{2-} + 3\ H_2O + 6\ e^- \qquad E^o = -598\ mV \qquad (71)$$

$$2\ S^{2-} + 6\ OH^- \rightarrow S_2O_3^{2-} + 3\ H_2O + 8\ e^- \qquad E^o = -612\ mV \qquad (72)$$

$$S^{2-} + 8\ OH^- \rightarrow SO_4^{2-} + 4\ H_2O + 8\ e^- \qquad E^o = -679\ mV \qquad (73)$$

Kinetic models based on kinetic control (reaction rate independent of S^{2-} concentration) and diffusion control (reaction rate dependent on S^{2-} concentration) were tested, to verify the kinetics of S^{2-}decay. To find the equations that best fit the experimental data, the model of partial order developed by Li et al. (2008) was used, where the reaction rate is proportional to $[S^{2-}]^n$ and dependent on the applied current, as represented in Eq. (74) and (75).

$$\text{reaction rate} = k\,[S^{2-}]^n i^m \qquad (74)$$

$$[S^{2-}]^{1-n}_{(t)} = [S^{2-}]^{1-n}_{(0)} - k(n\text{-}1)\,i^m\,t \qquad (75)$$

where, k is the kinetic constant, $[S^{2-}]$ is in mg L^{-1}, i is the applied current intensity in A, t is the time in h, and n and m are partial reaction orders. Since in each test the current intensity remained constant throughout the experimental period, as well as n, Eq. (74) and (75) can take the form of Eq. (76) and (77), respectively.

$$\text{reaction rate} = k'\,[S^{2-}]^n \qquad (76)$$

$$[S^{2-}]^{1-n}_{(t)} = [S^{2-}]^{1-n}_{(0)} - k'\,t \qquad (77)$$

where k' is a pseudo kinetic constant.

Analysis of $[S^{2-}]^n$ versus time, at constant current density, were carried out by varying n in steps of 0.01, up to the best correlation factor was obtained for each applied current density. For the tests run with 60 mM sulfide initial concentration, at different current densities, the optimal n values and the fitted equations are presented in Table 7 and Fig. 4, c and d.

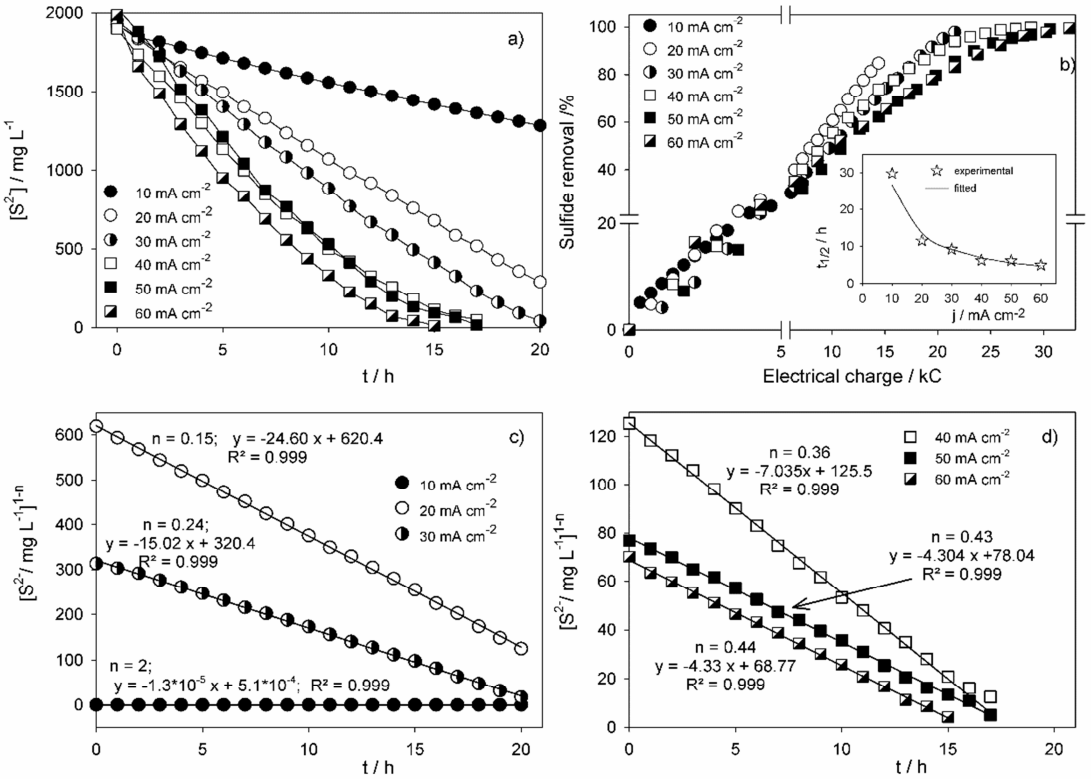

Figure 4. Sulfide removal at different applied current densities: a) Variation of the [S^{2-}] with time; b) Variation of the [S^{2-}] with electrical charge; Inset of b) Time needed for the removal of 50 % S^{2-} initial concentration; c) and d) $[S^{2-}]^{1-n}$ experimental data versus time and fittings to experimental data (Eq. 77). S^{2-} initial concentration of 60 mM.

The different orders found for the different applied current densities suggest that the kinetics of the S^{2-} oxidation is strongly influenced by the current density. For 10 mA cm^{-2}, the results showed a second order reaction related to S^{2-}. This behavior can be explained if it is assumed that the system was on kinetic control and the low flux of electrons prioritizes reactions involving few electrons, i.e., Eq. (47) and (48) or (54). The presence in these reactions of two S^{2-} species as reagent may explain the second order kinetics experimentally observed. The reaction scheme will slowly proceed with Eq. (54), (49) to (51), etc, due to the limited availability of electrons.

The increase in current density to the double, 20 mA cm^{-2}, reduces the meaning of the current control and gives more relevance to the S^{2-} diffusion. A further increase in the current density leads to an increase in the reaction order, showing that the system tends to be controlled by diffusion. Thus, oxidation was influenced by both the oxidation rate, kinetic control, and the diffusion rate of the substrate, diffusive control, as also observed by Haner et al. (2009) and Waterston et al. (2007).

Table 7. Reaction pseudo-orders for the kinetics of the [S^{2-}] decay at different current densities.

Current density / mA cm^{-2}	10	20	30	40	50	60
Reaction order -*n*	2.00	0.15	0.24	0.36	0.43	0.44

A value for the reaction order that is different from an integer is typically indicative of a complex mechanism that, in this case, must be a consequence of the competition between reactions, sometimes consuming S^{2-}, Eq. (47), (48), (66) and (67), among others, or consuming intermediate species derived from the previous reactions and competing for electric charges, Eq. (62) to (64) and (49), among others.

Considering the various presented possibilities for the S^{2-} oxidation, regarding the possible species formed, it was evaluated the behavior of S^{2-} during the oxidation process in relation to the SO_4^{2-} formation for the two extremes situations: a) transfer of 2 electric charges – oxidation of S^{2-} to S^0, reaction (47); b) transfer of 8 electric charges – oxidation of S^{2-} to SO_4^{2-}, Eq. (67) or (73). Figure 5 presents the hypothetical decays in [S^{2-}] if only extremes scenarios a) and b) were possible, as well as the real scenario. Scenarios a) and b) were calculated using the respective current intensities and Coulomb's law, Eq. (78).

$$q = i\,t \qquad (78)$$

where q is the electric charge, in C, i is the current intensity, in A, and t is in s.

According to Figure 5, a to f, the decrease in S^{2-} concentration showed intermediate behavior between the exclusive formation of elemental sulfur and the direct formation of SO_4^{2-}, i.e., the oxidation of S^{2-} occurs in steps in which the intermediate oxygenated species are formed and oxidized gradually until the final step represented by SO_4^{2-}. If there was a direct oxidation to SO_4^{2-}, the decrease in S^{2-} concentration would be less effective; on the other hand, if there was only oxidation of S^{2-} to elemental sulfur, the decay of the S^{2-} concentration would be dramatically higher. So, the reaction pathway involves the occurrence of the reactions described by Eq. (48) to (51), where the sulfur formed on the surface of BDD reacts with the S^{2-} producing S_x^{2-}. In fact, the formation of S_x^{2-} was observed, since the liquid phase presented a yellow color. However, polysulfides produced are consumed, producing SO_4^{2-} as a final step, explaining the loss of the yellow coloration.

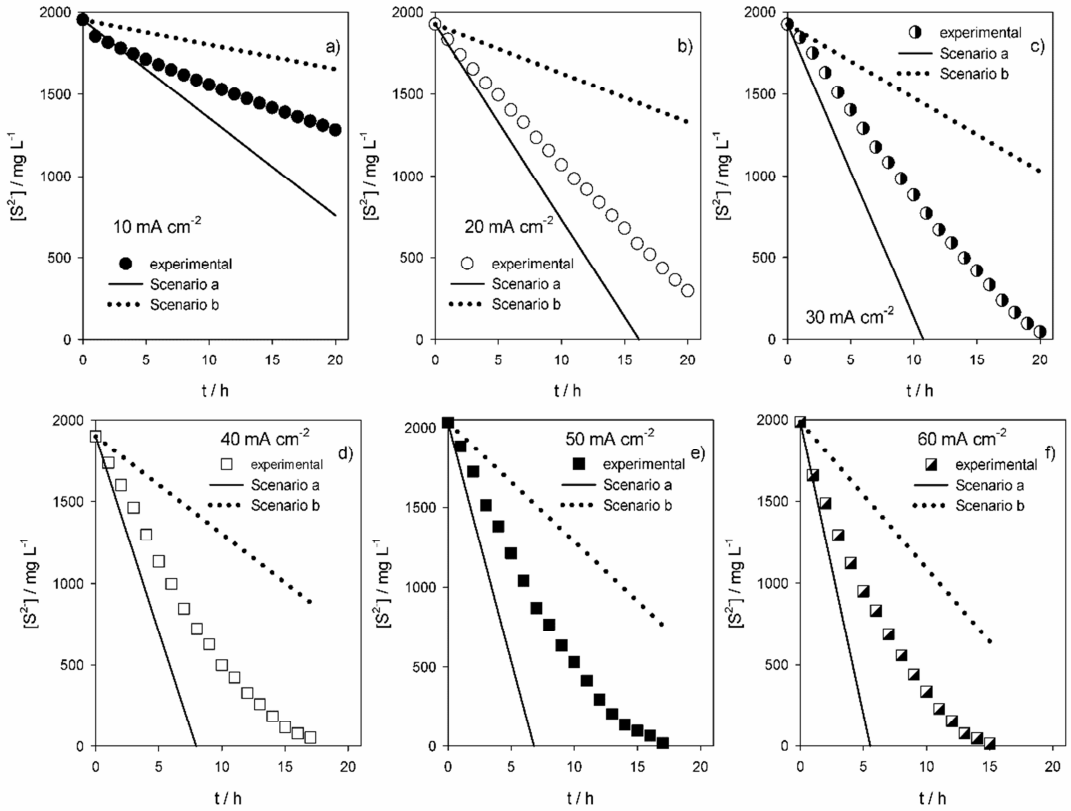

Figure 5. Variation of S^{2-} concentration with time in different scenarios: experimental (symbols); oxidation through Eq. (47) (scenario a); and oxidation through Eq. (67) or (73) (scenario b). Applied current densities of a) 10, b) 20, c) 30, d) 40, e) 50 and f) 60 mA cm^{-2}. S^{2-} initial concentration of 60 mM.

4.1.3 Sulfate formation

Regardless of the applied current density, in all the assays there was the formation of SO_4^{2-}. However, its formation rate is strongly influenced by the current density, with a linear behavior, as can be seen in Figure 6a for the initial S^{2-} concentration of 60 mM. The S^{2-} oxidation to SO_4^{2-} can happen either by direct oxidation, Eq. (67) or (73), or by indirect reactions, Eq. (66) followed by (64), and the greater the availability of electrons, the higher the sulfate formation rate. The linear equations adjusted to the experimental data up to the fifteenth hour of the assay are presented in Table 8.

To better understand the formation of SO_4^{2-} from the oxidation of S^{2-}, Eq. (79) was adjusted to the experimental data obtained for the SO_4^{2-} formation rate, being assumed that SO_4^{2-}-is obtained from S^{2-} oxidation and neglecting the formed intermediates.

$$\frac{d[SO_4^{2-}]}{dt} = k''[S^{2-}]^{n'} i^{m'} \quad (79)$$

where *k''* is a kinetic pseudo-constant for the sulfate formation, *n'* and *m'* are the reaction order for $[S^{2-}]$ and for current intensity, respectively.

By applying natural logarithm to Eq. (79) and using the Solver tool from Excel, the values of *k''*, *n'* and *m'* were calculated, using the experimental data for the variation of $[SO_4^{2-}]$and $[S^{2-}]$with time. The obtained values are presented in Table 8, except for n' that is equal to zero for all the applied current densities tested, and it can be observed that the sulfate formation is only dependent on the current density. Lower current densities originate lower SO_4^{2-} formation yield due to the current control and to the accumulation of intermediate species, such as S_2^{2-}, S_3^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and others.

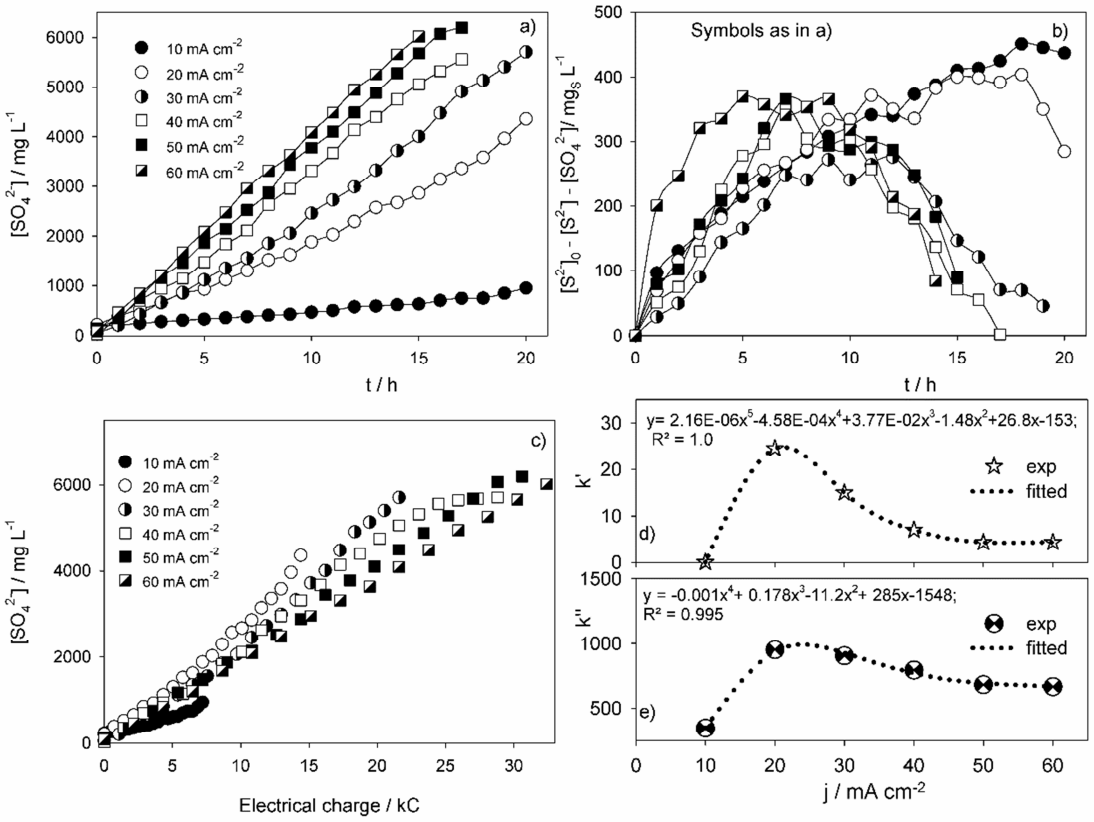

Figure 6. a) Evolution in time of the SO_4^{2-} formation for different applied current density; b) evolution in time of the sulfur species other than sulfide or sulfate, for different applied current densities; c) Variation of the sulfate formation with the electrical charge delivered; reaction pseudo-kinetic constants for the electro-oxidation of S^{2-} (d) and for the formation of SO_4^{2-} (e) from S^{2-} electro-oxidation for the different applied current densities.$[S^{2-}]_o$= 60 mM.

Table 8. Variation of sulfate concentration, in mg L^{-1}, with time, in h, and kinetic data, Eq. (79) for the formation of SO_4^{2-} from S^{2-} electro-oxidation, for different applied current densities

j / mA cm^{-2}	Adjusted equations	R^2	k" / mg L^{-1} h^{-1} A^{-1}	m'
10	$[SO_4^{2-}] = 30.47\ t + 178.6$	0.990	348	1.05
20	$[SO_4^{2-}] = 178.6\ t + 128.6$	0.993	951	1.00
30	$[SO_4^{2-}] = 264.6\ t - 146.3$	0.992	905	1.00
40	$[SO_4^{2-}] = 342.5\ t - 96.94$	0.996	794	1.00
50	$[SO_4^{2-}] = 374.5\ t + 3.217$	0.998	682	1.00
60	$[SO_4^{2-}] = 400.1\ t + 74.70$	0.999	667	1.04

To find out the amount of other sulfur oxidized species different from SO_4^{2-}, the variation of $[S^{2-}]_0 - [S^{2-}] - [SO_4^{2-}]$ was plotted against time (Fig. 6b), showing that the oxidation of S^{2-} may involve the formation of different species, besides the direct conversion into SO_4^{2-}. In fact, the oxidation conducted at 10 and 20 mA cm^{-2} showed the greatest differences in the mass balances, and persistently, indicating that the conversion of S^{2-} into SO_4^{2-} via anodic oxidation tends to present greater difficulties, because of the competition with the intermediate species by electrons.

For 20 mA cm^{-2}, the mass balance showed that consumption of S^{2-} was also followed by intense formation of intermediate species, with the maximum difference between the expected and the total sulfur formed at 18 h of run. Regarding the results for 30 mA cm^{-2}, the mass balance shows low oxidation to SO_4^{2-} until 7 h. Between 7 and 12 h, the accumulation of intermediates remained approximately constant, indicating an increase in their oxidation rate probably due to the decrease in the $[S^{2-}]$ after the 12 h assay.

For 40 and 50 mA cm^{-2}, the trend lines are similar to the assays performed at 20 and 30 mA cm^{-2}. This similarity in the intermediate species concentration between 20 and 50 mA cm^{-2} applied current densities doesn't necessarily means that the rate of SO_4^{2-} formation is equal, because $[S^{2-}]$ decay increases with current density and, consequently, if the intermediates concentration is equal the SO_4^{2-} formation must be higher for the highest applied current density.

The highest current density used in the last test, 60 mA cm^{-2}, showed a slightly different behavior. Apparently, the higher current intensity promoted more intense oxidation of S^{2-} in the first moments, i.e., generating appreciable concentrations of intermediate sulfur species. As can be seen in Figure 6b, at 5 h it was achieved the maximum concentration of those species, intensifying the competition between them and S^{2-}. After 5 h run, an enhancement of the intermediates oxidative process or a reduction on their formation rate is observed.

The current efficiency for the formation of sulfate from sulfide oxidation is depicted in Figure 6c, being the lowest efficiency observed for 10 mA cm^{-2}, probably because reactions involving lower number of electrons are favored, leading to low sulfate formation rate. On the other hand, the highest current efficiency regarding sulfate formation is observed for 20 mA cm^{-2}, since this must be the lowest current density that maintains the process in diffusional control, but with low oxygen evolution. For current density higher than 20 mA cm^{-2}, the process is clearly in diffusional control, wasting part of the applied current in oxygen evolution, which increases with applied current.

The influence of the applied current density on the direct formation of sulfate from sulfide can also be visualized in Figure 6, d and e, where the pseudo-kinetic constants *k'* and *k''*, obtained from data presented on Figure 4, c and d, and Table 8, are plotted against the current density. If data for 10 mA cm^{-2} is excluded, it can be observed that the decay in $[S^{2-}]$ is less influenced by changes in the applied current density than the sulfate formation rate, meaning that an increase in the current density will increase mainly the conversion of the intermediate species to sulfate rather than the oxidation of sulfide to intermediate species. The *k'* and *k''* values for 10 mA cm^{-2} can be explained by the low current intensity that greatly increases the current control.

4.1.4 Conclusions

The results obtained have proved that sulfide can be efficiently converted to sulfate by electrochemical oxidation using a BDD anode and that the process can be used to efficiently remove sulfide from effluents, even when its concentration is high. The following conclusions were also obtained:

- Oxidation of S^{2-} to SO_4^{2-} occurs in stages, characterized by the formation of sulfurous intermediate species, oxygenated or not, whose concentration tends to be lower with the increase in the applied current density.

- The oxidation of S^{2-} does not follow a single pathway, being dependent on the applied current density and presenting order 2 for the lower applied current density, which is compatible with a mechanism involving two S^{2-} ions to give S_2^{2-}. For higher applied current densities, where the current control is less important, the reaction order varies from 0.15 to 0.44 for the applied current densities of 20 and 60 mA cm^{-2}, respectively.

- The formation of SO_4^{2-} is strongly influenced by the applied current density, probably due to the involvement of hydroxyl radicals, and it is not dependent on the sulfide concentration.

4.2 Evaluation of the performance of three different electrode materials – BDD, Ti/Pt/PbO_2 and Ti/PtSnO_2-Sb_2O_4 - on the contaminants removal

The aim of this work was to evaluate and compare the efficiencies of different electrode materials, Ti/Pt/PbO_2, Ti/Pt/SnO_2-Sb_2O_4 and BDD, in the removal of carbonaceous and nitrogenous compounds from tannery effluents, simultaneously with the kinetic study of sulfide removal in the form of sulfate.

4.2.1 Experimental details

The electrodegradation assays were performed in batch mode for 8 h with constant stirring (100 rpm), using 250 mL of effluent collected in Curtumes Fabricio lda, Seia, Portugal. Ti/Pt/PbO_2, Ti/Pt/SnO_2-Sb_2O_4 (henceforth designated by PbO_2 and SnO_2, respectively) and BDD were used as anodes; a stainless steel foil was used as cathode. The electrodes of Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 (4 electrodepositions repetitions) were prepared as described in the literature (Andrade et al., 2007; Ciríaco et al., 2009; Santos et al., 2013).

The electrodes immersed areas were 10 cm^2, with an inter-electrode gap of 2 cm. Experiments were conducted at an applied current intensity of 0.3 A, at ambient temperature (22-25 ^oC), without the addition of supporting electrolyte. A power supply unit (Laboratory DC Power supply, Model GPS-3030D (0-30 V, 0-3 A) was utilized as power source.

For each experiment, 6 mL of sample were collected hourly to determine the proposed parameters: COD, TDC, DOC, TKN, TN, S^{2-}, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, NH_4^+, pH and conductivity.

4.2.2 Wastewater characterization

The analyzed effluent was produced in the washing process of the salted skins, and the samples used in this study were collected in an equalization basin, after a peroxide treatment, which aimed to oxidize the sulfide used in the skins' preparation process. The characteristics of the effluent are presented in Table 9.

The effluent contains a high organic load, which gives rise to high COD, DOC and TDC contents. The organic load is mainly due to fat, flesh, hair, skin, tallow and collagen fibers, derived from the skin cleaning process. Ammonium, nitrites and nitrates are low and the total nitrogen is almost only organic nitrogen, due to the presence of amino acids. Sulfide concentration is high, being one of the main problems of these effluents. It results from the skins pelage removal process, which utilizes sodium sulfide.

In the specific case of the effluent used in this study, since it was collected in a tank after the application of hydrogen peroxide, part of the sulfide was already oxidized to sulfate and,

thus, high concentration in SO_4^{2-} was expected. The high chloride concentration is due to the brine of the skins. The high pH value of 11.3 comes from the use of calcium oxide in the initial stages of the skins preparation process. Thus, the high value observed for the conductivity is derived from the several ionic species utilized during the initial procedures, previously cited.

Table 9. Physicochemical characteristics of the effluent.

Parameter	Average initialvalue (±SD[a])
COD / g L^{-1}	30 ± 1
TDC / g L^{-1}	7.95 ± 0.01
DOC / g L^{-1}	7.81 ± 0.01
NH_4^+ / mg L^{-1}	95 ± 4
NO_2^- / mg L^{-1}	5.0 ± 0.1
NO_3^- /mg L^{-1}	50 ± 3
TN / g N L^{-1}	2.98 ± 0.01
TKN / g N L^{-1}	2.81 ± 0.05
S^{2-} / mg L^{-1}	339 ± 1
SO_4^{2-} / g L^{-1}	2.16 ± 0.01
Cl^- / g L^{-1}	6.09 ± 0.04
pH	11.3 ± 0.1
Conductivity / mS cm^{-1}	26.7 ± 0.6

[a]Standard Deviation

The results presented in Table 9 may differ from others presented in the literature, because samples were collected in different parts of the effluents treatment plant: Kurt et al. (2007) and Apaydin et al. (2009) used the effluent obtained after the equalization basin; Szpyrkowicz et al. (2001) analyzed an effluent from an anaerobic treatment; Szpyrkowicz et al. (1995) and Song et al. (2001) worked with effluent collected after sedimentation tank; Rao et al (2001) used effluent gathered after secondary clarification stage; El-Sheikh et al. (2011) used effluent collected after a physicochemical treatment.

4.2.3 Organic load removal

The results of the organic load removal obtained in the electrodegradation assays performed at 30 mA cm^{-2}, with the different electrode materials, are presented in Figure 7. In the first four hours of the experiments, similar COD removals were attained with the different anode materials. After that time, higher removal efficiency was observed for the BDD electrode (Fig. 7a). At 4 hours assay, the COD removals were 29.6, 28.9 and 28.5% for BDD, PbO_2 and SnO_2, respectively, indicating the possibility of using metal oxides as a good alternative to BDD electrodes. For the total running time, 8 h, COD removals were 42.4, 34.7 and 35.8% for BDD, PbO_2 and SnO_2, respectively.

Regarding PbO_2 electrode, Rao et al. (2001) achieved higher COD removal rates than the obtained in this study. However, these authors used a tannery wastewater from secondary

clarifier with an average initial COD of 544 mg O_2 L^{-1}, much lower than the value observed in the effluent utilized in this study, 30 g O_2 L^{-1}. This may indicate the possibility of using metal oxides electrodes not only for degrading wastewater contaminants, but also as polishing step after biological treatment of the effluent.

In the removals of DOC (Fig. 7b) and TDC (data not shown) with the three electrode materials, BDD presented better results at the end of the 8 h assay, showing an augmented appetency for the mineralization of the organic compounds.

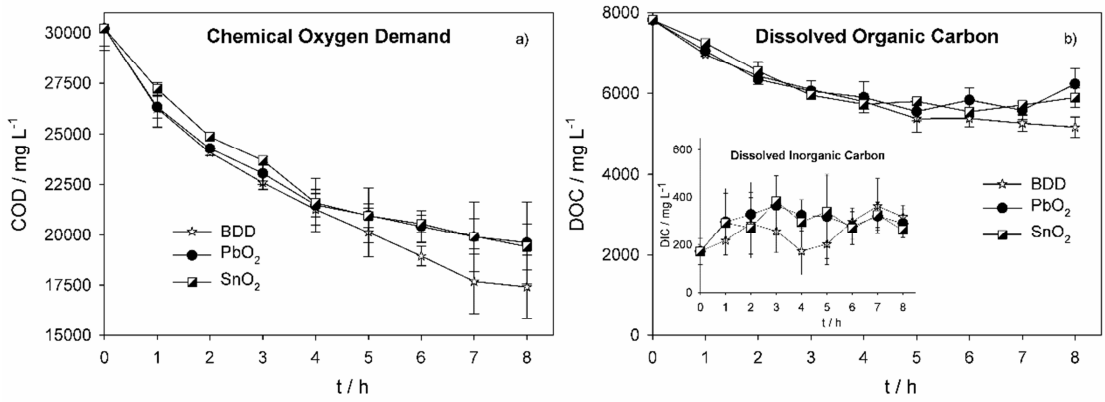

Figure 7. Variations in time of a) COD, b) DOC and (inset of b) DIC for the assays performed with the three electrode materials. I= 300 mA.

Considering that the oxidation of the organic matter present in effluents can occurs by direct or indirect oxidation, and although the effective degradation of contaminants is based on the direct electrochemical process and depends mainly on the reaction with $^{\bullet}OH$ radicals on the electrode's surface, the high Cl^- concentration in the samples (Table 9), the decays in COD, DOC and TDC along the treatment process and the characteristic strong odor of active chlorine during electrolysis, it appears evident the existence of simultaneous direct and indirect oxidation processes.

During the oxidation assays there are small variations in the DIC content (Fig 7b, inset), for all the tested anode materials. These variations must be mainly due to the progressive dissolution of the suspended solids present in the initial samples, process that must be also responsible for the low reductions in DOC observed during the 8th hour of the assays. This fact is not observed for COD, since DOC determinations are made with filtered samples and COD with non-filtered samples.

4.2.4 Nitrogen-containing compounds decay

Regarding TN removal, Figure 8a, the results show that the PbO_2 and SnO_2 electrodes tested led to similar yields (24%), being the results obtained with BDD slightly better (30%). The TN

reductions obtained with the metal oxides electrodes show that, in the case of this parameter, they can be used as a BDD alternative to remove nitrogen from wastewater.

The initial concentration of TN and TKN were very similar, being almost all TN oxidizable. Thus, the TN reduction, the NO_2^- constant concentration observed (about 5 mg L^{-1}, data not shown) and the limited production of NO_3^- (maximum 214.3 mg L^{-1} for BDD, Figure 8b) indicate that almost all TN removal was due to nitrogen losses in the gaseous form, such as N_2. However, the irregular variation presented by ammonia concentration points to a removal of the organic nitrogen by a mechanism that presents as first step its conversion to ammonia, followed by ammonia conversion to nitrogen gaseous forms or nitrate.

The formation of NO_3^-, Figure 8b, showed very distinct behaviors for the different anode materials, since during the assays the formation of this species was 214.3, 153.6 and 103.7 mg L^{-1}, for BDD, PbO_2 and SnO_2, respectively. Whereas BDD showed greater efficiency in the production of NO_3^-, SnO_2 was the least efficient in the N-containing compounds oxidation to NO_3^-. Thus, despite similar TN reductions provided by the three electrodes, BDD presents the highest ability to convert nitrogen to NO_3^-, whereas SnO_2 presents the lowest.

The loss in the ability for converting NH_4^+ to NO_3^- in the presence of Cl^- was also noted by Cabeza et al. (2007). According to these authors, Cl^- improves the efficiency for NH_4^+ removal but not its conversion to NO_3^-. However, it should be noted that in the case of SnO_2, the results showed that most of the nitrogen was converted to nitrogen gaseous species, which is an interesting situation because N and P are watercourses eutrophic agents, and the elimination of nitrogen from solution means that it will not be released into water bodies, thus reducing the potential for eutrophication.

The irregular variation for the NH_4^+ concentration obtained during the assays performed with BDD, PbO_2 and SnO_2 electrodes (inset of Figure 8a), which presents a residual value, shows a lower efficacy in eliminating NH_4^+ than that observed by Rao et al. (2001), in assays performed with smaller running times and lower current densities for an NH_4^+ initial content only slightly higher than the initial concentration of the samples used in this work (Table 9). However, the COD values for the samples used by Rao et al. (2001), around 500 mg L^{-1}, were much lower than the initial value of the effluent used in this study, 30 g L^{-1}. Thus, it can be seen that the NH_4^+ oxidation process observed by Rao et al. (2001) seems to have been intensified due to the low COD content of the samples. In the present study, the competition between organic matter and NH_4^+, due to the higher COD content, led to a decrease in the NH_4^+ oxidation rate.

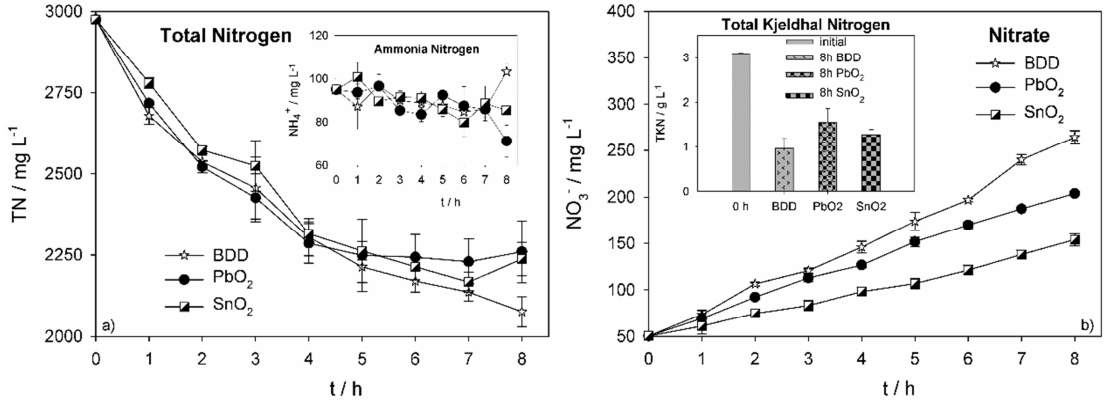

Figure 8. Variation in time a) TN, (inset of a) NH_4^+, b) NO_3^- and (inset of b) TKN for the assays performed with the three different electrode materials. I= 300 mA.

The NH_4^+ present in solutions containing Cl^- is indirectly oxidized according to Eq. (35) (Szpyrkowicz et al., 2001). This later explanation, and the proposed mechanism for the elimination of the organic nitrogen, already observed in different studies (Santos et al., 2010), may explain the irregular variation of the ammonia content.

Regarding TKN variation during the assays (inset of Figure 8b), BDD is the most effective anode for the oxidation of the organic nitrogen, followed by SnO_2 anode.

4.2.5 Sulfur compounds: S^{2-} and SO_4^{2-}

The results presented in Figure 9a show that S^{2-} removal by BDD electrode was higher than with the other two tested electrodes. After 8 hours, reductions in S^{2-} concentrations were 64.7, 44.1 and 27.9% for BDD, PbO_2 and SnO_2, respectively. Besides the different removal rates observed, a different removal dynamic for the three electrodes tested was also noted.

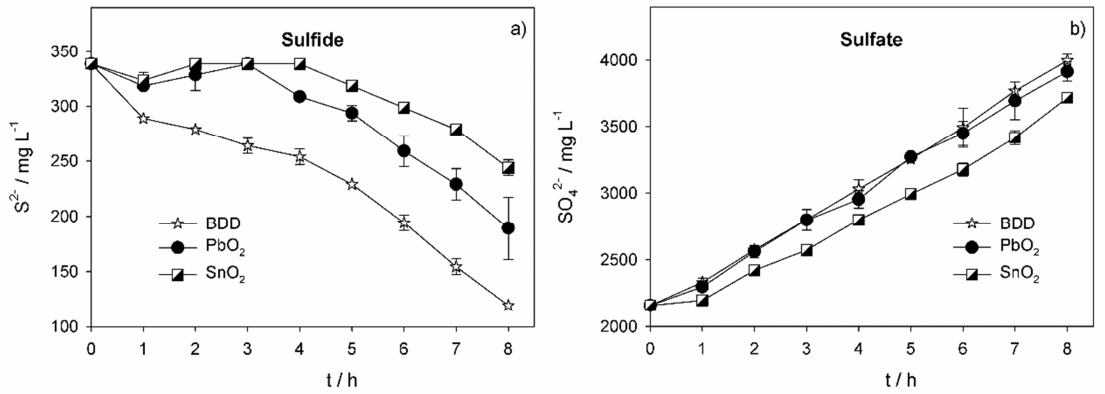

Figure 9. Variations of the concentration of a) S^{2-} and b) SO_4^{2-} during the assays run with the three different electrode materials. I= 300 mA.

At the beginning of run, BDD presented higher S^{2-} removal rate when compared with the other electrodes. After the fourth hour, the oxidation rate of S^{2-} at BDD showed an increase that was kept until the end of the experiment. The PbO_2 electrode provided reductions in the concentration of this parameter only after the third hour of the assay, and SnO_2 only after the fourth hour, the later with an apparent removal rate higher than that obtained with PbO_2 after that initial period.

According to the results, it seems that S^{2-} removal was limited by COD and TN contents, i.e., there is a priority in the removal, by electro-oxidation, of the different wastewater contaminants. In fact, the results showed that the removal of S^{2-} by BDD follows a trend in which is noted the inhibition of the S^{2-} oxidation by organic load and total nitrogen. However, from the fourth hour of the assays, COD/[S^{2-}] and [TN]/[S^{2-}] ratios reach the values of 84 and 9 (Figure 10, a and b) and S^{2-} oxidation become more intense. Apparently, there are limits of COD and TN concentrations, depending on the concentration of S^{2-}, from which the oxidation of S^{2-} tends to be more efficient. Similar situations were observed for the electrodes of PbO_2 and SnO_2.

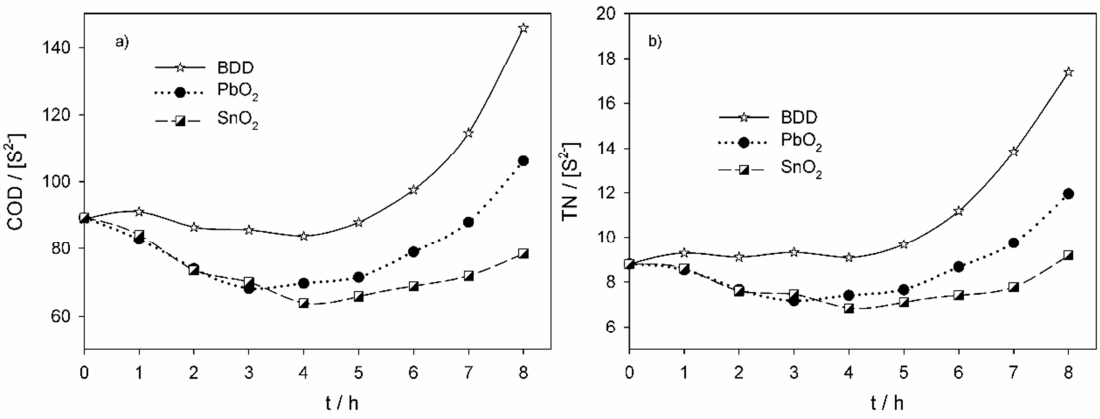

Figure 10. Values for the ratios a) [COD]/[S^{2-}] and b) [TN]/[S^{2-}] for the three electrode materials tested during the assays. I= 300 mA.

Regarding to the PbO_2 electrode, the boundary limits were 68 and 7 to [COD]/[S^{2-}] and [TN]/[S^{2-}], respectively. To the SnO_2 electrode, the boundary limits were 64 and 6.8. These results make clear the greater ability of BDD for the simultaneous removal of organic load, total nitrogen and sulfide. Thus, S^{2-} oxidation rate seems to be strongly limited by COD and TN, and this limitation is more intensely observed for the PbO_2 and SnO_2 electrodes.

For the SO_4^{2-} formation, Figure 9b, the behavior of the electrodes were similar to those found in the S^{2-} removal, that is, the best performance was observed by the BDD, followed by PbO_2 and SnO_2. Further analysis of the results showed a discrepancy between S^{2-} decay and SO_4^{2-}

formation, Table 10, presenting all the three electrodes formation of SO_4^{2-} amounts higher than expected based on S^{2-} consumption. This fact indicates that much of the sulfur in the system was in the form of structures with intermediate oxidation states between S^{2-} and SO_4^{2-}. Thus, the electro-oxidation promoted the oxidation to SO_4^{2-} of the S^{2-} and other sulfur species present in the samples.

Table 10. Values for the expected SO_4^{2-} formation, based on S^{2-}consumption, observed and the excess of produced SO_4^{2-}.

Electrode	S^{2-} consumed / mg L^{-1}	SO_4^{2-} expected / mg L^{-1}	SO_4^{2-} formed / mg L^{-1}	Excess / %
BDD	219.0	657.8	1838.2	179.4
PbO_2	149.3	447.9	1754.4	291.7
SnO_2	94.6	283.8	1558.2	449.0

4.2.6 pH, Conductivity and Electrical Potential

The results showed a reduction during the assays of the pH in the three systems tested, as can be seen in Fig. 11a. For BDD electrode, this situation appears to be associated with the occurrence of reactions shown by Eq. (41), (42) and (46). For the other two electrodes, equations (36), (37) and (38) may explain the phenomenon. Besides, the reactions (33), (35) and (40) also are associated with the pH reduction for all systems.

The strong chlorine odor found in the three systems, formed via Eq. (33), and the reduction in COD, DOC and TDC, Eq. (33) followed by (34) also appear to be involved in pH reduction. Similar analysis can be extrapolated for Eq. (35), related with ammonia oxidation. According to Panizza and Cerisola (2004), the initial pH is an important parameter in indirect electrochemical processes because it influences the activity of chlorine and its oxidation potential. In fact, the electrogenerated chlorine can disproportionate, forming hypochlorous acid, Eq. (33), which is converted to hypochlorite ions, by Eq. (40).

Furthermore, the higher COD removal obtained with BDD is mainly related with Eq. (41) and (42), justifying the larger pH drop for the sample treated by this electrode.

Regarding the variation of the conductivity during the assays, Figure 11b, the higher increase occurred for BDD and may be explained by the higher reduction observed in COD, as well as, higher NO_3^- formation, etc. In fact, the formation of smaller particles will increase the value of the conductivity.BDD electrode was also the material that presented the highest initial potential difference, 7.5 V, compared to the other two electrodes tested, PbO_2, 5.9 V, and SnO_2, 6.7 V, Figure 11c. Similar results were found by Fernandes et al. (2014) in the electro-oxidation of landfill leachate. According to these authors, this situation is due to the higher conductivity of the metal oxides electrodes when compared to BDD.

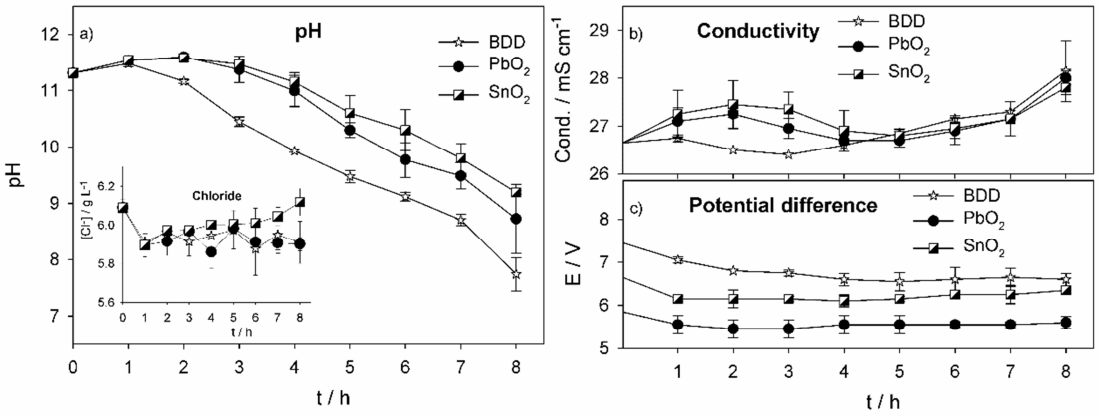

Figure 11. Variation of a) pH, (inset of a) chloride concentration, b) conductivity and c) potential difference for the assays performed with the three different electrode materials. I= 300 mA.

In all systems, it was noted a reduction in the potential during the assays. According to Costa et al. (2008), the electrode potential reduction occurs due to the increasing conductivity of the samples along the assay. The reduction in the electrical resistance of the system appears to be derived from the increase in ionic species and small molecules formed during the elimination and/or conversion of contaminants that also contribute to the increase in conductivity of the samples. Thus, it appears that BDD has a higher efficiency, given the higher increase in the potential reduction observed for this material. This is in line with its great ability for oxidation of wastewater contaminants.

4.2.7 Specific Charge Consumption

To analyze the effect of different electrode materials, the specific charge consumption, SC, in C (g of removed COD)$^{-1}$, was determined by Eq. (80). For S^{2-}, C (g of removed S^{2-})$^{-1}$; for SO_4^{2}-, in C (g of formed SO_4^{2}-)$^{-1}$.

$$SC = \frac{i\,t}{(COD_n - COD_m)\,V} \qquad (80)$$

where *i* is the current intensity, in A, *t* is in s, and COD_n and COD_m are COD values, in g L^{-1}, at time *n* and *m*, respectively, and *V* is the volume, in L. As can be seen in Figure 12, the results showed that for 8 h assay BDD presented the lowest energy consumption. However, for the first three hours of the assays, the charge consumption for the different electrodes was very similar, around 1.77 kCg^{-1} COD removed, indicating the possibility of the application of metal oxide electrodes as an alternative to BDD in the COD removal from tannery effluents.

Regarding S^{2-} removal, the results showed that in addition to providing the greatest reduction of this contaminant, BDD presented the lowest power consumption, as can be seen in Table 11, showing a great ability for S^{2-} removal from tannery wastewater. However, when the energy consumption for the SO_4^{2-} formation is evaluated, the results show that, although SnO_2 energy consumption is higher, SnO_2 led to the increased formation of SO_4^{2-} based on S^{2-} consumed, as described above. This situation shows that although SnO_2 electrode presents higher power consumption than BDD, it presented higher ability to produce SO_4^{2-} from S^{2-} and other various sulfur species.

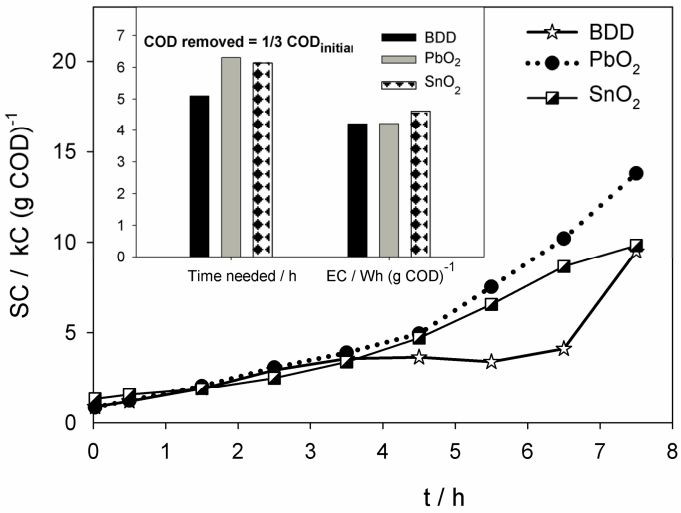

Figure 12. Charge consumption for the three different anodes during the electro-oxidation assays and (inset) time needed to attain the removal of 1/3 of the initial COD and energy consumed in this process. I= 300 mA.

Table 11. Specific charge consumption for COD and S^{2-} removal and SO_4^{2-} formation.

Electrode	Specific charge consumption (kC g^{-1})		
	COD consumed	S^{2-} consumed	SO_4^{2-} formed
BDD	2.70	157.81	18.80
PbO_2	3.25	231.40	19.70
SnO_2	3.21	365.33	22.18

4.2.8 Conclusions

The results obtained show that:

- BDD proved to be more efficient in the removal of COD and TDC without, however, presenting different behavior from the two other electrodes with respect to DOC removal;

- Although SnO_2 electrode has smaller ability for conversion of nitrogen forms into NO_3^-, it presents as an interesting alternative for the removal of this contaminant by converting the organic nitrogen to gaseous N-containing compounds, which is very interesting to avoid eutrophication of the water bodies;

- Whereas BDD acts intensively on the S^{2-} oxidation to SO_4^{2-}, promoting this conversion at higher initial rates than the other tested electrode materials, after a time interval, rates become similar. In some cases, the oxide metal electrodes present even higher sulfide oxidation rates, showing the possibility of their application in the treatment of tannery wastewater for S^{2-}removal. This is interesting because they are less expensive materials than BDD;

- In addition to greater ability for COD removal, BDD presented also the lowest energy consumption.

4.3 Chemical or electrochemical coagulation with aluminum combined with anodic oxidation at different electrode materials

The aim of this study was to evaluate and compare the efficiencies of different electrode materials, SnO_2, PbO_2 and BDD, in the removal of carbonaceous and nitrogenous compounds from tannery effluents previously clarified by chemical coagulation, with aluminum salts, or by electrochemical coagulation with aluminum sacrificial anodes. In addition, the kinetic study of sulfide removal in the form of sulfate during anodic oxidation assays of tannery wastewater samples pretreated with chemical coagulation or electrocoagulation, by aluminum cations, was also assessed.

4.3.1 Experimental details

Before the sample's clarification by chemical coagulation, the determination of the best dosage of clarifier $Al_2(SO_4)_3$ was carried out in a Jar Test equipment, Lovibond Floc tester ET 730. Samples (0.4 L) were tested for different Al^{3+}concentrations, 0.25, 0.5, 1.0, 2.0 and 4.0 g L^{-1}, for three different hydrodynamic conditions, as shown in Table 12. All tests were run in duplicate.

Table 12. Hydrodynamic conditions for the clarification tests.

Operation	Condition 1	Condition 2	Condition 3
	time (/min) / stirring rate (/rpm)		
rapid mixing	1 / 100	2 / 200	3 / 200
slow mixing	15 / 20	15 / 20	15 / 20
sedimentation	120 / 0	120 / 0	120 / 0

After each clarification test, the determination of residual turbidity was carried out using a digital turbidimeter Orbeco-Hellige 965-10. The dosage of clarifier that generated lower residual turbidity was defined as the best concentration for the clarification stage. Once determined the best clarifying conditions, sufficient quantities of samples were obtained to perform the anodic electro-oxidation steps with SnO_2, PbO_2 and BDD anodes.

To evaluate the performance of the clarifications by chemical coagulation and electrocoagulation, the raw effluent was also subjected to clarification by electrocoagulation. In this step, aluminum plates were used as cathode and anode. The electrodes were separated by 2 cm, with 20 cm of immersed areas each one. The EC was performed with 0.4 L of sample volume, contained in 0.6 L glass beakers, placed in the Jar Test. The stirring rate was 20 rpm. The EC time was similar to that one used in the mixing process of the CC assays; the applied electric current was the sufficient to reach the best

clarifier concentration determined for the CC assays. The assays were repeated until enough clarified samples were produced for the electro-oxidation tests to be run with SnO_2, PbO_2 and BDD anodes.

The electro-oxidation assays were conducted in batch mode, for 8 h with constant stirring (100 rpm), using 400 mL of clarified sample at room temperature (22-25 ^oC) without adding any electrolyte. SnO_2, PbO_2 and BDD electrodes were used as anodes; a stainless steel plate was used as cathode. The anode and the cathode were separated by 2 cm, having 10 cm^2 of immersed area each one. The electric current used was 0.3 A. A power supply unit (Laboratory DC Power Supply, GPS-3030D model (0-30 V, 0-3 A)) was used as the power source.

For each oxidation assay, 12 mL of sample were taken in intervals of 2 h to determine the proposed parameters: COD, DOC, TDC, DIC, TKN, TN, N-NH_3, S^{2-}, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, Al^{3+}, pH and conductivity. The samples subjected to determination of aluminum concentration were those pre- and post-clarified (0 h), and collected at 4 and 8 h of the anodic oxidation assays.

4.3.2 Wastewater characterization

Table 13 shows the results for the raw wastewater characterization, collected in the equalization tank of a tannery industry, Curtumes Fabricio lda, Seia, Portugal. The effluent contains mostly organic compounds, such as fats, meat, hair, skin, fat and collagen fibers derived from the skin cleaning process, which directly contribute for the COD, TDC, DOC and TN parameters. The presence of S^{2-} results from the process of hair removal that uses sodium sulfide. For this reason, high S^{2-} concentration was observed in the samples.

Table 13. Physicochemical characteristics and parameters concentrations for raw effluent and after CC and EC assays, with respective standard deviations. Conductivity is in mS cm^{-1}; all other parameters, except pH, are in mg L^{-1}.

Parameter	Raw sample	After CC	After EC
pH	9.0 ± 0.1	7.6 ± 0.0	9.9 ± 0.1
Conductivity	20.4 ± 0.0	21.1 ± 0.2	18.6 ± 0.1
COD	5,326 ± 73	3,354 ± 85	3,423 ± 35
DOC	1,332± 6	982 ± 27	1,051 ± 15
TDC	1,562 ± 14	1,094 ± 39	1,164 ± 17
DIC	233 ± 4	116 ± 8	116 ± 8
N-NH_3	328 ± 6	311 ± 7	287 ± 16
TKN	468 ± 5	357 ± 2	354 ± 4
TN	489 ± 1	413 ± 6	406 ± 8
S^{2-}	165 ± 4	114 ± 2	110 ± 3
NO_3^-	20 ± 2	30 ± 9	16 ± 2
NO_2^-	< 5.0	< 5.0	< 5.0
SO_4^{2-}	1,053 ± 8	2,380 ± 23	910 ± 27
Al	8 ± 3	2.4 ± 0.3	20 ± 2
Cl^-	5,306 ± 96	5,223 ± 35	4,881 ± 13

The high Cl^- concentration observed in the initial effluent results from the leather processing process, since it is previously salty. The initial pH value, 9.3, results from the use of calcium oxide in the initial stages of the preparation process of the skin. The high conductivity is derived from the various substances used during the procedures previously cited.

The reasons why the results of the effluent characterization differ substantially from those presented in the literature were already discussed in section 4.2.2 of this thesis.

4.3.3 Influence of clarifier concentration and hydrodynamic conditions on the clarification process

The results from the effluent clarification tests are shown in Table 14. It was found that the clarification efficacy was influenced by the concentration of the clarifying agent, reaching the maximum efficiency for Al^{3+} concentration of 0.5 g L^{-1}. The increase in turbidity observed at concentrations higher than 0.5 g L^{-1} was due to the loss of clarification efficiency, because excess coagulant reverses the neutralization of the surface charge of suspended particles, preventing the coagulation (Duan and Gregory, 2003).

Table 14. Turbidity values with standard deviations obtained for the different hydrodynamic conditions (Table 12) used in clarification tests by CC.

$[Al^{3+}]$ /g L^{-1}	Turbidity (NTU)		
	Condition 1	Condition 2	Condition 3
0.0	2,530 ± 42	2,520 ± 240	2,726 ± 35
0.25	80 ± 28	44 ± 1	50 ± 2
0.5	6 ± 1	6 ± 1	6.5 ± 0.7
1.0	72 ± 10	73 ± 6	72 ± 26
2.0	532 ± 9	489 ± 32	440 ± 13
4.0	681 ± 42	684 ± 69	701 ± 90

Regarding the hydrodynamic characteristics of the process, there were no significant influences. Considering the residual turbidity and the fact that condition 1 requires less energy consumption (rapid mixing step), the anodic oxidation assays were performed with clarified samples under this condition, utilizing an Al^{3+} concentration of 0.5 g L^{-1}.

4.3.4 Clarification assays

Given the conclusions obtained in the previous subsection for the best experimental conditions to perform CC, the experimental conditions set for EC assays were the following: an EC time of 18 min, similar to that one used in the mixing process of the CC assays; an applied electric current of 1.98 A, needed to introduce in the raw effluent an aluminum amount similar to that used in CC experiment during the 18 min.

The experimental results obtained in the clarification assays showed no significant differences between the CC and the EC clarification processes for COD removal (Table 13). The COD removal for CC and EC were 37% (1,972 mg L^{-1}) and 36% (1,903 mg L^{-1}), respectively. This shows the feasibility of applying any of the two processes tested for the effluent clarification. Nevertheless, the clarification of wastewater by using aluminum, either CC or EC, presents a large drawback that is the formation of sludge rich in this metal, because it is a toxic metal.

Table 13 shows that approximately 85% of TDC was organic carbon. This was expected, since the effluent used in this study was a newly generated effluent. Furthermore, approximately 30% (468 mg L^{-1}) of TDC was removed in the CC step. Regarding DOC, the clarification assay by CC and EC reached removals of 26% (350 mg L^{-1}) and 21% (281 mg L^{-1}), respectively, Table 13. Although it was used the same concentration of Al^{3+} (0.5 g L^{-1}) in both cases, these differences can be derived from a better operational control in CC process than in EC. The best operational control in clarification by CC can explain the change in the aluminum concentration from raw to after CC and after EC, Table 13, because it decreased from 8 to 2.4 mg L^{-1} for CC, whereas for EC an increase in its concentration was observed, with 20 mg L^{-1} as final value.

The N-NH_3 removals were low: 5.2% (17 mg L^{-1}) for CC and 12.5% (41 mg L^{-1}) for EC. This reduced efficacy in the N-NH_3 depletion during coagulation/flocculation happens because of ammonia solubilization. A different situation was observed for TKN, since the removals by CC and EC were 23.8 and 24.3%, respectively. These values were very similar to those verified for DOC. This shows that the fall in TN concentration during coagulation/flocculation for tannery wastewater treatment is mainly derived from TKN removal and occurs parallel to DOC removal.

The results for S^{2-} removal, Table 13, showed that the two applied clarification methods, CC and EC, presented similar efficiencies in the removing of S^{2-}, 30.9% (51 mg L^{-1}) and 33.3% (55 mg L^{-1}), respectively. As it was expected, reductions in the S^{2-} levels by aluminum cation were much lower than those observed in the literature when iron cation is used. The low efficiency of aluminum for S^{2-} removal, if compared with iron, is easily evidenced by Eq. (5), since the solubility of the product formed, Al_2S_3, is not as low as that observed for the Fe_2S_3, Eq. (6).

The increase in SO_4^{2-} concentration during clarification by CC , from 1,053 to 2,380 mg L^{-1} (+ 126%) was expected, since it was used $Al_2(SO_4)_3$ as clarifier agent. For the samples clarified by EC, significant differences between the initial and final SO_4^{2-} concentration were not verified. This evidences that the EC is not a good process for SO_4^{2-} removal.

The reduction in the chlorine concentration, when comparing values for Raw and after EC clarification samples, appears to be associated with the EC process itself, since the oxidation at the anode can produces Cl_2, Eq. (32), that induces Cl^- consumption.

4.3.5 Electro-oxidation

4.3.5.1 Carbonaceous compounds

The anodic oxidation of the clarified samples from CC and EC showed similar results in all tests for COD removal, Table 15. However, at the end of the 8 h of AO, the samples clarified by CC and oxidized using PbO_2 and BDD anodes showed substantial difference from the value observed for the SnO_2 anode for COD removal, 40% (1,344 mg L^{-1}), 41% (1,366 mg L^{-1}) and 31% (1,035 mg L^{-1}), respectively.

The observed results for COD removal for the CC+AO and CE+AO sets were higher than those observed for anodic oxidation of not clarified samples. This situation demonstrates once again the possibility of use of AO as polishing step in the treatment of tannery industry effluents, and the importance of the pretreatment as factor for the best performance of the oxidation system.

Table 15. Final concentrations in COD and DOC (mg L^{-1}), with standard deviations, after 8 h AO assay for the samples pretreated with clarification by CC or EC and for the raw sample.

Electrode	Pretreatment					
	CC	EC	Raw	CC	EC	Raw
	COD			DOC		
SnO_2	2,319 ± 17	2,296 ± 47	3,323 ± 62	951 ± 4	924 ± 13	1,186 ± 23
PbO_2	2,010 ± 46	2,181 ± 31	3,097 ± 40	897 ± 5	916 ± 9	1,106 ± 32
BDD	1,988 ± 49	2,058 ± 20	2,717 ± 141	773 ± 13	797 ± 2	1,021 ± 27

Regarding DOC removal, the results obtained with BDD for the clarified (CC or EC) and unclarified samples are better than those obtained with SnO_2 and PbO_2 electrodes, Table 15. This situation is consistent with the high oxidant capacity of the BDD, compared with the other two tested electrodes, and demonstrates its ability to eliminate organic carbon.

For the anodic oxidation of the unclarified sample, the best performance in DOC removal was presented by the BDD electrode, 23.4% removal (311 mg L^{-1}). However, only the DOC removal during clarification by the CC was higher, 26.3% (350.0 mg L^{-1}), Tables 13 and 15. This situation confirms the limited capacity of AO, since the verified DOC removal by CC was greater than that observed for the best electrode, the BDD. On the other hand, if considered the CC+AO set for BDD, the total DOC removal increased to 40% (535 mg L^{-1}). Thus, despite its limitation, the data confirm that the AO can be studied as a polishing step in the treatment of pre-treated tannery effluent, e.g., by CC.

According to Vlyssides and Israilides (1997), the effective degradation of the organic matter present in effluents is based on the direct electrochemical process and depends mainly on the reaction with $^{\bullet}OH$ radicals on the electrode's surface, Eq. (41). Besides, the BDD anode presents an overvpotential for O_2 evolution, much higher than the conventional anodes,

producing large amounts of adsorbed $^{\bullet}OH$, Eq. (41), and thereby resulting in a rapid and effective pollutants degradation (Palma-Goyes et al., 2010). These observations can explain the greatest removal of COD by BDD.

Further analysis showed that, for all samples, the TDC and DOC removals were not similar during the AO assay, with a slight advantage for the TDC removal, since the relationship between [TDC]/[DOC] decreased, as can be seen in Table 16. Thus, although the AO process has shown good performance for TDC removal, in special for DIC removal, it did not present the same efficiency in the DOC elimination.

Table 16. [TDC]/[DOC] ratio for AO assays. Duration: 8 h.

Pretreatment	Time / h	[TDC]/[DOC]		
		SnO_2	PbO_2	BDD
Raw	0	1.2	1.2	1.2
	8	1.0	1.0	1.0
CC	0	1.1	1.1	1.1
	8	1.0	1.0	1.0
EC	0	1.1	1.1	1.1
	8	1.0	1.0	1.0

The high Cl^- concentration in the samples, Table 13, the COD, TDC and DOC removals in the process and the strong characteristic odor of active chlorine, showed the participation of chlorine, and its derivatives, in the removal process of the organic matter, through indirect oxidation. However, according to Vlyssides and Israilides (1997), whereas the active chlorine can act as a mediator for wastewater treatment, Eq. (81) and (82), it is unable to completely oxidize the organic compounds. Thus, it can be inferred that the observed depletion in the DOC concentration was almost exclusively derived from the reactions occurring on the surface of the electrodes, Eq. (31).

$$R + Cl_2 + e^- \rightarrow RCl + Cl^- \quad (81)$$

$$RCl + OH^- \rightarrow RO + Cl^- + H^+ + e^- \quad (82)$$

4.3.5.2 Nitrogen compounds

The results showed high efficacy of BDD in the removal of ammonia nitrogen for all the tested samples. The SnO_2 electrode presented the lowest performance, Table 17. However, for the three tested electrodes, the ammonia nitrogen removal during AO was substantially lower for the raw effluent than for the clarified effluent. This situation seems to be derived from the competition for the electric charges by the organic load, Eq. (31), and the Cl^-, to form Cl_2 and HOCl, Eq. (32) and (33), respectively, with posterior attack to the organic contaminants, Eq.

(34), since in these cases, the sample had large organic load. Thus, it is clear the negative influence of the organic load in the ammonia removal by anodic oxidation. The NH_4^+ present in solutions containing Cl^- is indirectly oxidized according to Eq. (35).

Table 17. Final concentrations (mg L^{-1}), with standard deviations, of TN, TKN, N-NH_3 and NO_3^- for clarification by CC and EC, and for raw sample, after 8 h of AO assay.

Parameter	Pretreatment	Electrode		
		SnO_2	PbO_2	BDD
TN	Raw	278 ± 5	237 ± 17	217 ± 9
	CC	238 ± 9	213 ± 8	154 ± 6
	EC	225 ± 2	178 ± 8	206 ± 13
TKN	Raw	225 ± 19	190 ± 5	136 ± 12
	CC	195 ± 6	164 ± 7	54 ± 10
	EC	179 ± 2	135 ± 5	108 ± 1
N-NH_3	Raw	149 ± 9	120 ± 12	70 ± 7
	CC	120 ± 8	100 ± 6	26 ± 4
	EC	123 ± 6	120 ± 12	57 ± 9
NO_3^-	Raw	142 ± 5	185 ± 2	406 ± 13
	CC	161 ± 2	210 ± 10	467.9 ± 0.8
	EC	100 ± 8	185 ± 11	419 ± 24

The ammonia nitrogen reductions found by Rao et al. (2001) were much higher, even with lesser running time and current densities. At the end of 4 h and using current densities ranging from 6.7 to 16.7 mA cm^{-2}, the NH_4^+ removals were between 48.1 and 81.2% for an initial concentration between 102 and 105 mg L^{-1}, just above the concentration in this work. However, the COD concentration in Rao et al. (2001), presented values between 520 and 544 mg L^{-1}, much lower than in this work, 5,326 mg L^{-1}. Thus, it can be concluded that the oxidative processes for NH_4^+ removal, observed in the Rao et al. (2001) study, were intensified due to the low COD concentration, i.e., the decrease in competition between organic carbonated matter and Cl^- for the electric charges due to the low COD concentrations have led to more intense oxidative activity of NH_4^+.

The observed results for ammonia oxidation open an interesting possibility of AO application for post-treatment of anaerobic steps, because this system, besides removing organic load, also promotes the conversion of organic nitrogen into ammonia nitrogen, which could facilitate the nitrogen removal in the case of a posterior AO treatment. Moreover, the reduction in nitrogen load in the effluent limits its eutrophic ability for water courses. Although, in general, the BDD electrode has better yields, the results showed that the anodic oxidation by PbO_2 and SnO_2, when applied to clarified effluent, can satisfactorily remove the ammonia nitrogen.

Further analysis showed that the Kjeldahl nitrogen removal was more intense than that observed for TN, for all electrodes, Table 17, i.e., Kjeldhal nitrogen oxidation occurred more intensively than the loss of nitrogen as N_2, Eq. (35), or other gaseous forms of nitrogen. In addition, BDD electrode showed the best TKN capacity removal when compared to the other two tested electrodes. Table 18 presents TN/TKN ratios for the different assays and it can be observed that there is an increase in this ratio, in particular for the assays run with BDD anode.

Regarding the reductions in TN concentrations for the three tested electrodes during the anodic oxidation tests, Tables 13 and 17, BDD presented the best performance, followed by PbO_2 and SnO_2. BDD electrode also presents greater capacity for conversion of ammonia nitrogen into nitrates, since these parameters present the highest values for the electro-oxidation performed with this anode, being $SnO_2$the electrode with the low stability for the conversion of ammonia to nitrate. During all the assays, NO_2^- concentrations below 5 mg L^{-1} were found.

Table 18. [TN]/[TKN] ratio for AO assays. Duration: 8 h.

Pretreatment	Time / h	[TN]/[TKN]		
		SnO_2	PbO_2	BDD
Raw	0	1.0	1.0	1.0
	8	1.2	1.3	1.6
CC	0	1.2	1.2	1.2
	8	1.2	1.3	2.8
EC	0	1.1	1.1	1.1
	8	1.3	1.3	1.9

4.3.5.3 Sulfide removal and Sulfate formation

Results obtained for the anodic oxidation of the clarified samples showed that after 4 hours the S^{2-} ion was completely eliminated, Figure 13a. This shows that the tested electrodes have similar efficiencies for sulfide removal, showing that PbO_2 and SnO_2 anodes can be used for S^{2-} removal from effluents with similar concentrations to those observed in this study.

Regarding S^{2-} removal, there is no advantage of sample clarification, since after 4 h of AO of raw samples there was no noticeable S^{2-} concentrations.

The SO_4^{2-} concentrations increased over the time, Figure 13b, with a tendency to stabilize after 8 h of assay, showing the scarcity of SO_4^{2-} precursor species. It was also found that the SO_4^{2-} final concentrations were much higher than the initial S^{2-} concentration. Detailed analysis showed that the conversion S^{2-}/SO_4^{2-} presented peculiar characteristics. As it can be seen in Table 19, the three electrodes produced SO_4^{2-} quantity above the predicted, based on

S^{2-}availability. This situation shows that the SO_4^{2-} formation is due to S^{2-} oxidation, oxidation of intermediate sulfur species derived from S^{2-}, originally present in the samples, and also from organic sulfur.

When comparing the results for clarified samples, the samples clarified by CC presented lower SO_4^{2-} formation than those clarified by EC, Table 19. Such a situation is probably due to a more intense removal of existing sulfur species in the clarification by CC. It seems that the best CC operational control provided better performance, which can facilitated the removal of these species, with lower formation of SO_4^{2-} during AO. In the case of wastewater treatment process optimization, this seems to be very interesting, since removing almost total S^{2-} and sulfur species by CC reduces competition for electrical charges, favoring the removal of carbonaceous and nitrogenous contaminants.

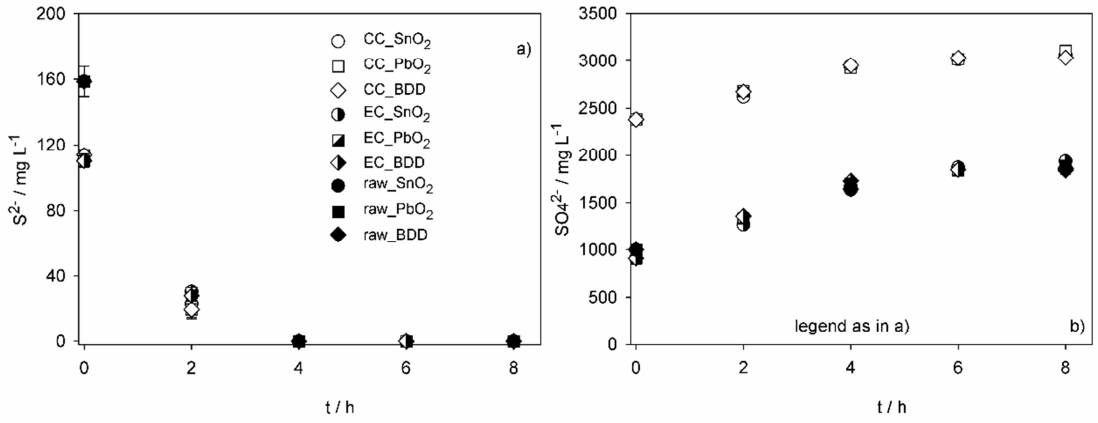

Figure 13. Changes in the concentrations of a) S^{2-} and b) SO_4^{2-}during AO, performed with the three electrodes, for clarified and unclarified sample. Duration: 8 h.

For all the series, the final SO_4^{2-} concentrations obtained for SnO_2 and PbO_2 electrodes were similar to those observed for BDD, indicating the possibility of using metal oxide electrodes, like SnO_2 and PbO_2, to replace BDD in the conversion of species containing sulfur into SO_4^{2-} in the electrochemical oxidation of tannery effluents.

Table 19. SO_4^{2-} concentrations (mg L^{-1}), formed and expected for all anodic oxidation assays, considering S^{2-} ion available. Duration: 8 h.

SO_4^{2-}	CC			EC			without clarification		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
Formed	686.0	726.0	653.0	1027.0	978.0	949.0	863.0	879.0	842.0
Expected	341.1	341.1	341.1	330.3	330.3	330.3	475.5	475.5	475.5

4.3.5.4 Chloride, Conductivity, pH and Potential

The Cl^- concentrations decreased over the experiments, Figure 14a, independently of the process. This situation seems to be associated with the loss of Cl^- as Cl_2, Eq. (32), since it was observed the occurrence of a strong odor to Cl_2 during the assays.

For all the tests, Figure 14b, BDD was the electrode material that systematically presented the highest potential. Similar results were found by Fernandes et al. (2014) during tests with the same electrodes in the electro-oxidation of landfill leachate and were attributed to the higher conductivity of the metal oxides when compared to BDD.

For all samples submitted to electro-oxidation by SnO_2 and PbO_2, clarified or not, it was not found any trend in the potential variation. However, with BDD a clear reduction in the potential throughout the assays was observed, as can be seen in Figure 14b. According to Costa et al. (2008), reductions in the potential occur due to the increase in sample's conductivity. This reduction appears to be derived from the increase in the number of ionic species and small molecules formed due to the initial pollutants electrodegradation.

The decrease in the initial conductivity for samples pretreated with EC, when compared with the initial conductivity for raw sample, Figure 14c, appears be derived from the electrocoagulation process itself, since the reactions occurring in the system, reduction and oxidation reactions, can change the molecular structure of some contaminants, promoting the reducing in conductivity.

About pH, the results demonstrated a decrease of this parameter in all the tests, as can be seen in Figure 14d. For BDD, this situation seems to be associated with the occurrence of the reaction represented by Eq. (41). For the other two electrodes, Eq. (36) to (38) can explain this situation.

The chlorine strong odor for all three systems showing its formation, Eq. (32), followed by Eq. (33), associated with COD, DOC and TDC reductions, Eq. (34), also seem to be related to the pH reduction. The same analysis can be extrapolated to the Eq. (35), related to the reduction of nitrogen load.

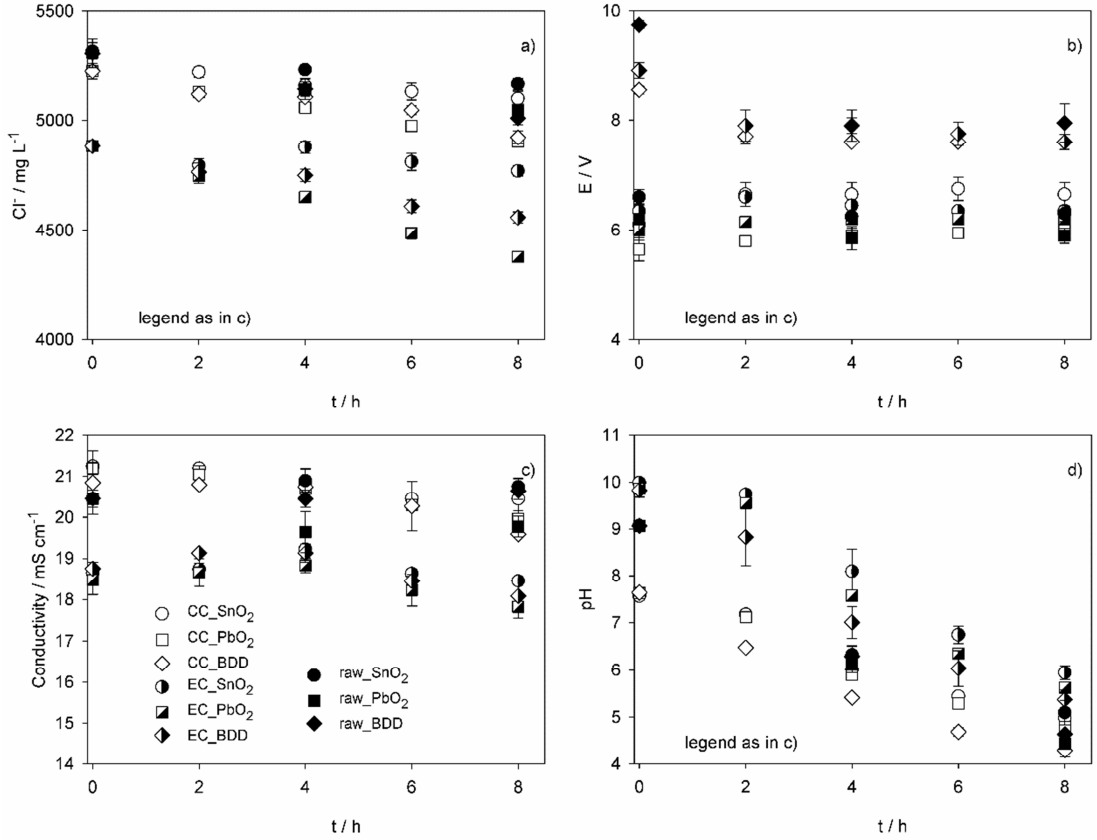

Figure 14. Variations of: a) chloride concentration; b) potential; c) conductivity and d) pH for all the AO assays performed at the 3 electrode materials, using samples with different pretreatments. Duration 8 h.

4.3.5.5 Specific Charge Consumption

Equation (80) was used to analyze the effect of the different electrode materials on the specific charge consumption.

For all the samples submitted to AO, BDD electrode showed the lower energy consumption for COD, DOC and TKN removals, Table 20, independently of the pretreatment. According to the literature, such situation is derived from its higher oxidation ability, compared to the other electrode materials. In general, SnO_2 and PbO_2 electrodes presented higher energy consumption for clarified samples, suggesting that the energy efficiency of these electrodes is more strongly influenced by the contaminant concentration than for the BDD electrode, since the energy consumption for clarified samples were always much higher than that observed for non-clarified samples.

In general, COD, DOC and TKN removals were accompanied by lower energy consumption for the samples clarified by EC than clarified by CC, Table 20. This must be due to some partial oxidation of contaminants during EC, potentiating the oxidation by AO, the last step.

Table 20. Average specific energy consumption for 8-h AO assays: For COD, DOC and TKN - kC/g removed; for SO_4^{2-} - kC/g formed. Duration: 8 h.

Parameter	CC			EC			raw		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
COD	22.7	16.1	14.9	19.4	16.8	16.1	10.4	9.4	8.0
DOC	351.2	287.0	114.4	154.8	183.1	83.6	167.4	103.3	73.5
TKN	131.6	111.4	71.9	120.5	100.6	87.2	89.5	78.2	65.4
SO_4^{2-}	31.5	29.8	33.1	21.0	22.1	22.8	25.0	24.6	25.7

As for the specific charge consumption, the energy values for SO_4^{2-} formation are aligned with the comments about S^{2-}/SO_4^{2-} conversion, since it was found higher quantity formed than the expected for the SO_4^{2-} ion, featuring the BDD electrode as the most efficient in the S^{2-} removal, but not in the SO_4^{2-} production. An opposite situation can be found for SnO_2 and PbO_2 electrodes.

The COD removal, at the time interval from 0 to 4 h, occurred with the highest removal rates. At the same time, the best energetic efficiency for all systems was observed and, in general, the BDD electrode showed superior performance, Table 21. This situation was expected, since at this time interval there were high contaminant concentrations, i.e., the system worked under a typical kinetic control. In fact, if the intervals 0 to 4 h and 4 to 8 h are compared, from 4 to 8 h, the energy consumption for all sets increased between 26 and 73%, with small removal rates, Tables 20 and 21. Thus, it is clear that a typical diffusional control become more important during the second part of the assays.

The energy consumptions for COD removals were always lower than those observed for the other parameters, regardless the time interval considered, 4 or 8 h. Thus, this situation demonstrates that this parameter is easily removed, but not necessarily indicates facility for DOC removals, since the energy consumptions for DOC removals were always much higher than those observed for COD removal.

Regarding energetic efficiency for DOC removal, the opposite effect was observed, Tables 20 and 21, since in the time interval from 4 to 8 h, in general, there was a decrease in the specific charge consumption, with the PbO_2 electrode showing the highest drop. The observed drop in specific charge consumption for DOC removal seems to indicate that COD is more easily removed than DOC. This means that organic matter is mainly converted to small oxidized molecules instead of being eliminated as CO_2.

Table 21. Specific Energy Consumption during AO assays. For COD, DOC and TKN: kC/g removed; for SO_4^{2-}: kC/g formed considering the first 4 hours.

Parameter	post CC			post EC			without clarification		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
COD	17.5	12.8	11.4	11.5	11.5	11.8	6.0	5.6	5.6
DOC	375.7	411.4	108.5	241.3	389.2	83.4	119.7	110.5	77.7
TKN	198.8	196.2	110.4	270.7	181.3	93.9	91.5	56.3	78.0
SO_4^{2-}	19.7	19.9	18.9	14.9	13.7	13.2	16.2	15.5	16.8

The comparison of specific charge consumption for TKN removal for the time intervals 0 to 4, Table 21, and 4 to 8 h show an increase in energetic efficiency, Table 20, since there was decrease with time of the specific charge consumption for all clarified samples. This situation characterizes the difficulty for TKN removal, when compared with COD removal. In other words, the COD acts like a limiting factor for a better TKN removal, showing that the process has a priority sequence for contaminants removal, as can be seen in figures 15a and 15b. The same scenario was not observed for unclarified samples.

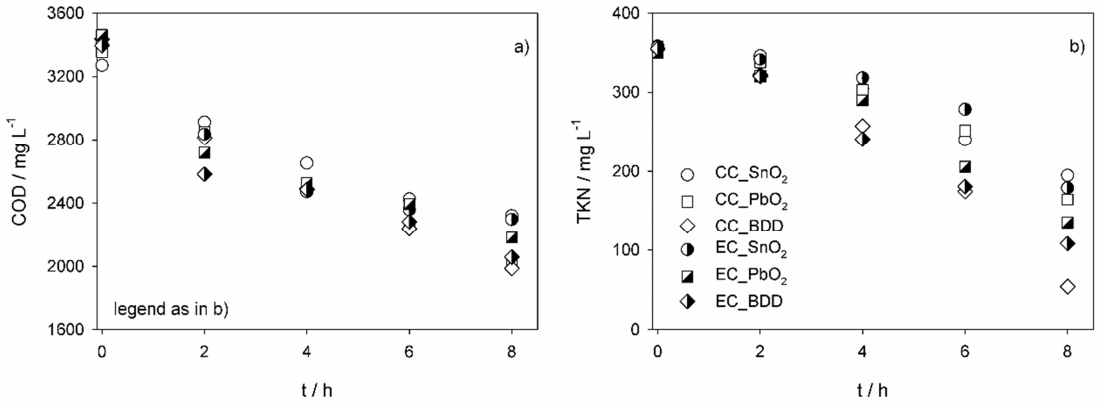

Figure 15. Changes in the concentrations of a) COD and b) TKN during AO assays for all tested sets for clarified. Duration: 8 h.

4.3.6 Conclusions

The obtained results led to the following conclusions:

- The chemical coagulation with aluminum proved to be more efficient than the electrocoagulation to clarify the samples and reduce the levels of contaminants. This may be associated with better management of operating conditions in chemical coagulation system than those applied to electrocoagulation systems;

- Regardless of the process, the clarification of effluent proved to be a useful pretreatment for tannery wastewater, since it can remove efficiently part of the organic load;

- The energy consumption in the anodic oxidation processes performed with SnO_2 and PbO_2 anodes is more strongly influenced by the contaminants concentrations than for the BDD anode;

- The BDD proved to be very efficient in the NH_4^+ removal, which promoted reduction in TKN concentrations through conversion of NH_4^+ to NO_3^- for both clarified and non-clarified samples;

- The greatest ability of BDD electrode in S^{2-} oxidation is not reflected in the conversion of this species into SO_4^{2-}. In fact, the SnO_2 electrode, although present low S^{2-} oxidation ability, is more efficient in the conversion of intermediate species containing sulfur into SO_4^{2-}.

4.4 Chemical or electrochemical coagulation with iron combined with anodic oxidation at different electrode materials

The aim of this work was to evaluate and compare the efficiencies of different electrode materials, SnO_2, PbO_2 and BDD, in the removal of carbonaceous and nitrogenous compounds from tannery effluents pretreated with chemical or electrochemical coagulation, with iron ions. The effect of biological activities on the efficiency of clarification process and of anodic oxidation was also assessed.

4.4.1 Experimental details

Raw tannery effluent was collected in the equalization tank of a tannery industry, Curtumes Fabricio lda, Seia, Portugal. To check the effect of biological activities on the efficiency of the clarification process and anodic oxidation, the sample was used as collected, SA, and part of the raw material was stored in an open container without aeration system for 10 days at room temperature, 22-27 ^{o}C, to give a different sample, SB. SA and SB samples were subjected to the treatments described below.

SA: Clarification by chemical coagulation with $FeCl_3$, followed by anodic oxidation using SnO_2 or PbO_2 electrodes as anodes.

SB: a) Clarification by chemical coagulation with $FeCl_3$, followed by anodic oxidation using SnO_2 or PbO_2 electrodes as anodes.

b) Clarification by electrocoagulation using iron electrodes, followed by anodic oxidation with PbO_2, SnO_2 and BDD electrodes.

c) Anodic oxidation with PbO_2, SnO_2 and BDD electrodes.

The experimental details for these assays were as described in section 4.3.1, Table 12, being $Al_2(SO_4)_3$ replaced by $FeCl_3$.

4.4.2 Wastewater characteristics

Table 22 shows the results obtained in the characterization of both wastewaters utilized in this study, SA and SB. The effluent contains mostly organic compounds, such as fats, meat, hair, skin, tallow and collagen fibers derived from the skin cleansing process, which directly interfere with the COD, TDC, DOC and TN parameters. As referred before, the characterization results differ substantially from the literature, because the characteristics of the samples are strongly influenced by the operating conditions of leather production systems and the moment of taking the sample

The higher initial pH, 11.3, stems from the use of calcium oxide – lime (CaO) in the initial stages of the processing of the skin. The high conductivity observed is derived from the various substances used during the initial procedures previously cited.

Table 22. Physicochemical characteristics of the effluent analysed with respective medium values and standard deviations. Conductivity in mS cm^{-1}; all other parameters, except pH, in mg L^{-1}.

Parameter	SA	SB
pH	11.6 ± 0.0	8.2 ± 0.2
Conductivity	12.5 ± 0.0	15.5 ± 0.2
COD	9,982 ± 142	9,905 ± 37
DOC	2,950 ± 27	3,066 ± 120
TDC	2,980 ± 33	3,269 ± 116
DIC	25 ± 1	216 ± 14
NH_3-N	70 ± 8	602 ± 6
TN	1,057 ± 23	1,050 ± 13
TKN	1,030 ± 8	1,042 ± 12
S^{2-}	110 ± 4	76 ± 1
NO_3^-	23 ± 3	23 ± 4
NO_2^-	< 5.0	< 5.0
SO_4^{2-}	1,314 ± 25	1,314 ± 25
Fe	24 ± 2	24 ± 2
Cl^-	2,868 ± 16	2,802 ± 44

The results showed no significant influence of biological action on the concentration of COD for SB, despite having affected other parameters. Considering that the system has not been aerated, the main biological activities that took place were anaerobic. Thus, the unchanged COD appears to be associated with the consumption of carbonaceous matter for the proliferation and maintenance of microorganisms, retaining thereby the carbon available in the system.

The effects of the biological activities in the effluent SB resulted in the increase of conductivity and inorganic carbon concentration and the decrease of pH and S^{2-} concentration. The decrease in S^{2-} concentration happens due to the decrease in pH, because the formation of this ionic specie is favored at high pH values. It is important to note that the absence of additional aeration to the SB promoted the conversion of the organic nitrogen into N-NH_3, not into NO_3^-. The formation of NO_3^- from organic nitrogen is expected only in aerated systems.

The results showed a decrease of 30.5% in S^{2-} concentration for sample SB (110 to 76 mg L^{-1}). According to USEPA (1985), S^{2-}solutions can contain three sulfur chemical species, S^{2-}, HS^- and H_2S, equations (83) and (84), and the species concentrations depend heavily on the system pH.

$$H_2S \leftrightarrow HS^- + H^+ \quad (83)$$

$$HS^- \leftrightarrow S^{2-} + H^+ \quad (84)$$

Thus, whereas pH increase promotes S^{2-} formation, pH reductions lead to its consumption and H_2S formation. In this case, due to a decrease in pH from 11.6 to 8.2, H_2S was produced and released by the system, causing S^{2-} concentration depletion.

4.4.3 Influence of clarifier concentration and hydrodynamic conditions on clarification process

The results from the effluent clarification tests are listed in Table 23. As it can be seen, the clarification efficiency and lowest residual turbidity were influenced by the concentration of the clarifying agent, reaching maximum efficiency for iron concentration equal to 1.0 mg L^{-1}.

Table 23. Residual turbidity with standard deviation after clarification by CC to the different hydrodynamics conditions. For the different conditions, see Table 12.

Fe^{3+} / g L^{-1}	Turbidity (NTU)		
	Condition 1	Condition 2	Condition 3
0.0	1,810 ± 184	1,810 ± 184	1,810 ± 184
0.5	428 ± 60	164 ± 42	152 ± 138
1.0	19 ± 4	10 ± 3	8.0 ± 0.0
2.0	529 ± 37	482 ± 32	459 ± 27
4.0	206 ± 36	123 ± 7	106 ± 6

The increase in turbidity for concentrations higher than 1.0 mg L^{-1} was due to the loss of clarification efficiency, since an excess of coagulant reverses the neutralization of surface charges of the suspended particles and promotes a negative impact in the clarification (Duan and Gregory, 2003).

The decrease on the residual turbidity when the iron concentration was changed from 2 to 4 mg L^{-1} was derived from the intensification of the sample color by adding coagulant. The iron cation (Fe^{3+}) is brown and increases the color of the solution. This interferes in the determination of the turbidity, because the scattered light is absorbed by the sample before reaching the sensor that captures the scattered light. In fact, Teixeira and Caliari (2005) found that the increase in the sample's color was accompanied by a reduction in turbidity.

Regarding the hydrodynamic characteristics of the process, it was found that increasing the time in rapid mixing it increases the efficiency of the clarification process, as already observed by Dharmappa et al. (1993).

4.4.4 Clarification assays

Table 24 presents the results obtained for SA after CC and SB after CC and EC.

Table 24. Physicochemical parameters and concentrations of the pretreated effluent, after CC and EC assays, with respective standard deviations. Conductivity in mS cm^{-1}; all other parameters, except pH, in mg L^{-1}.

Parameter	SA	SB	
	After CC	After CC	After EC
pH	3.8 ± 0.0	5.9 ± 0.0	7.9 ± 0.1
Conductivity	16.2 ± 0.1	16.8 ± 0.2	14.3 ± 0.6
COD	1,735 ± 21	5,312 ± 70	6,566 ± 84
DOC	586 ± 15	1,748 ± 44	2,241 ± 205
TDC	599 ± 14	1,785 ± 48	2,453 ± 34
DIC	12.0 ± 0.4	38 ± 3	113 ± 13
$N\text{-}NH_3$	49.4 ± 0.7	575 ± 14	535 ± 24
TN	260 ± 2	847 ± 15	809 ± 39
TKN	239 ± 18	832 ± 53	757 ± 22
S^{2-}	4.0 ± 0.7	3.7 ± 0.5	17.2± 0.0
NO_3^-	33 ± 2	34 ± 3	28 ± 2
NO_2^-	<5.0	<5.0	<5.0
SO_4^{2-}	1,246 ± 1	1,247 ± 17	1,425 ± 14
Fe	3 ± 1	2.5 ± 0.2	42 ± 13
Cl^-	5,085 ± 24	5,109 ± 32	2,592 ± 28

The samples SA and SB clarified by CC showed a different behavior due to the biological activity suffered by SB. The removals in COD for pretreated SA and SB were 82.6% (8,247 mg L^{-1}) and 46.3% (4,593 mg L^{-1}), respectively. This means a loss in clarification efficiency of 44.0%. This situation was due to the biodegradation of the contaminants present in the sample, converting the suspended organic matter into soluble organic matter, hindering the removal by sedimentation. Thus, these results show a negative effect of the biological activity for samples to be clarified by CC.

For sample SB, CC was more efficient in COD removal than EC probably because CC allows better operating control than EC.

Regarding DOC removal, the clarification by CC of SA and SB samples reached removal rates of 80.1% (2,364 mg L^{-1}) and 43.0% (1,318 mg L^{-1}), respectively. The SB clarification by EC presented DOC removal of 26.9% (825 mg L^{-1}). The removal rates obtained in the clarification of SB by EC, once again, show the harmful effect of the biological activities, particularly the dissolution of organic carbon in the liquid phase, when the objective is to remove the organic matter applying clarification as pretreatment.

The SA clarification by CC showed that the carbonaceous compounds, measured as TDC and DOC, were basically organic carbon, since the observed removal of these parameters were 2,381 and 2,364 mg L^{-1}, for TDC and DOC, respectively, Tables 22 and 24. In addition, the TKN

must be essentially suspended material, because its reduction was 792 mg L^{-1}. The same scenario was not observed for SB, where the TDC and DOC concentrations were reduced in 1,484 and 1,318 mg L^{-1}, respectively, while the TKN was reduced in 209 mg L^{-1}. These situations resulted from the solubilization of large quantity of TDC and the conversion of TKN into N-NH_3 by the biological activities.

Data in Tables 22 and 24 show that CC was more efficient in the S^{2-} removal when compared with EC, since the S^{2-} removal by CC attained index of 96.4% (106 mg L^{-1}) and 95.2% (73 mg L^{-1}) for samples from SA and SB, respectively. The EC reached 77.5% (59 mg L^{-1}) as maximum reduction in S^{2-} concentration in the sample SB. Reductions in S^{2-} levels in the samples can be explained by Eq. (10). Also, due to the coexistence of the HS^- and S^{2-} species, the sulfide can be removed according to equations (11) and (13).

The reduction in the pH after CC resulted from the Fe^{3+} hydrolysis, Eq. (7), (8) and (9).

4.4.5 Anodic oxidation

4.4.5.1 Carbonaceous compounds

The anodic oxidation of the sample from SA clarified by CC (SA_CC) showed similar results with SnO_2 and PbO_2 electrodes after 8-h assays, with removals of 812.1 and 724.9 mg L^{-1}, respectively, Tables 24 and 25. This shows the similar efficiencies of these electrodes in the removal of COD. For the samples SB submitted to EC (SB_EC) there was a small loss in efficiency of SnO_2 and PbO_2 electrodes, with removals of 702.9 and 606.8 mg L^{-1}, respectively. This loss in efficiency seems to be associated with the low yield in the clarification provided by electrocoagulation, if compared with that obtained by chemical coagulation that increases competition by the electric charges.

In the AO of SB_EC, BDD anode was more efficient than PbO_2 and SnO_2 anodes in the COD removal, since removal was 1,995.6 mg L^{-1}, i.e., approximately 3 times higher than COD removal by PbO_2 and SnO_2 electrodes. For unclarified sample (SB_raw), the COD reductions provided by BDD, SnO_2 and PbO_2 electrodes were 3,101.8, 2,482.1 and 2,633.6 mg L^{-1}, respectively, showing the best performance of BDD.

The results for DOC and TDC removals for SB_EC and SB_raw showed identical behavior to that of COD. Anyway, the clarification of the sample, in special by CC, tends to improve the performance of the anodic oxidation, namely of metal oxide electrodes, like SnO_2 and PbO_2.

The overpotential for O_2 evolution presented by BDD anodes, which produces large amounts of adsorbed $^{\bullet}OH$, Eq. (41), and thereby resulting in a rapid and effective pollutants degradation can explain the greater removal of COD by BDD (Palma-Goyes et al. 2010).

Table 25. Final concentrations (mg L^{-1}), with standard deviations, for COD, DOC, TDC, N-NH_3, TKN, TN, NO_3^- and SO_4^{2-}, for samples clarified by CC and EC, and for SB raw sample, after 8 h of AO assay.

Parameter	Electrode	Sample			
		SA_CC	SB_CC	SB_EC	SB_raw
COD	SnO_2	923 ± 28	----	5,863 ± 14	7,423 ± 49
	PbO_2	1,010 ± 52	----	5,959 ± 28	7,271 ± 81
	BDD	----	3,604 ± 85	4,571 ± 38	6,803 ± 50
DOC	SnO_2	407 ± 6	----	2,164 ± 20	2,659 ± 43
	PbO_2	441 ± 14	----	2,179 ± 22	2,580 ± 13
	BDD	----	1,350 ± 69	1,534 ± 11	2,339 ± 4
TDC	SnO_2	409 ± 1	----	2,156 ± 14	2,693 ± 49
	PbO_2	458 ± 12	----	2,163 ± 17	2,610 ± 18
	BDD	----	1,364 ± 41	1,860 ± 21	2,378 ± 2
N-NH_3	SnO_2	0	----	438 ± 7	501 ± 2
	PbO_2	0	----	446 ± 15	442 ± 11
	BDD	----	293 ± 6	358 ± 17	446.7 ± 0.8
TKN	SnO_2	51 ± 10	----	621 ± 6	710 ± 10
	PbO_2	56 ± 1	----	620 ± 14	686 ± 7
	BDD	----	346 ± 32	467 ± 49	680 ± 14
TN	SnO_2	78 ± 4	----	755 ± 13	893 ± 23
	PbO_2	85 ± 9	----	749.1 ± 0.9	877 ± 1
	BDD	----	488 ± 15	652 ± 38	904 ± 15
NO_3^-	SnO_2	140 ± 6	----	144 ± 7	132 ± 14
	PbO_2	130 ± 9	----	100 ± 2	99 ± 5
	BDD	----	248 ± 10	369 ± 6	417 ± 14
SO_4^{2-}	SnO_2	1,345 ± 6	----	1,529 ± 46	1,530 ± 3
	PbO_2	1,330 ± 13	----	1,536 ± 20	1,526.5 ± 0.5
	BDD	----	1,317 ± 15	1,493 ± 24	1,465 ± 20

It is worth noting that for sample SB_raw after 8 hours of anodic oxidation the maximum DOC removal efficiency was observed for the BDD electrode, 23.7% (726 mg L^{-1}), Tables 22 and 25, whereas only the CC of the same sample showed removal of 1,318 mg L^{-1}, Tables 22 and 24. These results again demonstrate the feasibility of using a CC pretreatment in the effluent treatment process of the tannery industry. This situation seems to be interesting, because, according to Bengtsson and Tillman (2004), Axelrad et al. (2013) and Toumi et al. (2015), the sludge generated in the clarification can be applied as a soil fertilizer, promoting agricultural production.

The high concentration of Cl^- in the samples, Table 22, and its behavior during the anodic oxidation tests, the reductions in COD, DOC and TDC concentrations, and the strong characteristic odor of active chlorine during electrolysis showed the participation of chlorine, through indirect reactions, equations (81) and (82), in the organic matter removal. The final TDC results for AO are presented in Table 25.

4.4.5.2 Nitrogenous matter

For the samples from SA anodically treated by SnO_2 and PbO_2 it was observed total N-NH_3 elimination after 6 and 8 h assay, respectively, Table 25, i.e., the two electrodes showed similar behavior in the N-NH_3 removal. This may be associated not only to the low concentrations of this contaminant, 49 mg L^{-1}, Table 24, but also the possible participation of Cl^-. According to Szpyrkowicz et al. (2001), NH_4^+ present in solutions containing Cl^- is oxidized indirectly from Eq. (35).

In fact, the low N-NH_3 concentration in SA seems to be the main factor involved in the total N-NH_3 removal, since in the SB sample the initial N-NH_3 concentration was 535 mg L^{-1}, Table 24, and the final concentration oscillated between 358 and 438 mg L^{-1} for the three tested electrodes, Table 25, i.e., the maximum removal was 178 mg L^{-1}. The loss in efficiency for N-NH_3 removal seems to be associated with the high concentration of carbonaceous matter present in the SB sample submitted to EC, Table 24, because this condition tends to intensify the competition by electrical charges, reducing N-NH_3 removal rates.

Indeed, the results showed similar efficiency for N-NH_3 removal for the three tested electrodes for unclarified samples, since the removals for BDD, SnO_2 and PbO_2 were 25.9, 16.8 and 26.6%, respectively, values very similar to those observed for SB_EC submitted to AO, 33.2, 16.2 and 16.7%, respectively, for the same electrodes.

Although, in general, BDD leads to better yields, the results showed that the anodic oxidation with SnO_2 and PbO_2, when applied to newly produced tannery effluent, i.e., without the application of biological treatment, and previously subjected to CC by $FeCl_3$, can satisfactorily remove the N-NH_3. However, this situation is conditioned in the absence of biological activities, in which case the organic nitrogen can be converted to N-NH_3 (anaerobic activities), which compromises the removal by CC and AO. In this case not even the BDD could remove completely the N-NH_3.

The results showed that TKN removal was very similar to N-NH_3 removal, for the same samples. However, the relationship between TKN and N-NH_3 did not change in the same way during assay for the three tested electrodes. In fact, when comparing TKN and N-NH_3 in SB_EC before and after AO, Tables 24 and 25, it is clear that TKN reduction was higher than N-NH_3 decrease, i.e., the AO promoted the elimination not only of N-NH_3, but of the organic nitrogen too. Moreover, the biggest difference was noted for the BDD electrode, i.e., the BDD

electrode presented higher eliminating ability of N-NH_3, it also eliminated more intensely the organic nitrogen from the sample, indicating its great oxidation capacity. The same situation was not verified for unclarified samples. This seems to be associated with the high contaminants concentrations in this system, which provides greater competition by electrical charges.

The observed TN removals, which may be associated with the elimination of N-NH_3, Eq. (35), were similar for the three electrodes for unclarified sample, Table 25. For SB_EC after AO, the BDD electrode showed significant difference when compared to SnO_2 and PbO_2, 19.4 against 6.8 and 7.4%, respectively. These results are compatible with the higher production by BDD anode of adsorbed $^{\bullet}OH$, which results in a rapid and effective pollutants degradation. The results of SA coagulated samples showed that the addition of an extra step in the treatment of tannery wastewater tends to be very favorable, since the removal of 75.4% of TN in CC stage, associated with anodic oxidation reached final levels higher than 92.0% for SnO_2 and PbO_2 electrodes, demonstrating the feasibility of using these electrodes.

The results for NO_3^- formation from SB_raw and SB-EC show that during the anodic oxidation step BDD electrode is the most efficient, followed by SnO_2 electrode and PbO_2. Once more, this situation seems to result from the high $^{\bullet}OH$ production by BDD anode that oxidizes the reduced species to the highest oxidation, as in the case of NO_3^-.

As can be seen in Table 25, for BDD there was lower NO_3^- production in AO of SB_CC. This result shows that the formation of NO_3^- is influenced by NH_4^+ consumption, and this formation is strongly, negatively, influenced by the presence of Cl^-, because this ion is converted to HOCl, Eq. (32) followed by Eq. (33), which reacts with NH_4^+ forming N_2, equation (35), rather than NO_3^-. This situation was also noted by Cabeza et al. (2007). Thus, the results of the combined treatment CC+AO show an excellent alternative to nitrogen load removal. This is very interesting, because if the final effluent presents nitrogen load still not fully oxidized, there will be the consumption of dissolved oxygen in the system. On the other hand, if the nitrogen loading is oxidized, for example, in the form of NO_3^-, there will be an undesirable situation, because the nitrogen is one of eutrophying agents, together with phosphorus, of watercourses. So, maximizing the elimination of nitrogen load there will be a significant and positive impact on water quality of watercourses.

For all assays the NO_2^- concentrations were below 5 mg L^{-1}.

4.4.5.3 Sulfur compounds

The anodic oxidation results for the samples subjected to CC or EC showed that after 2 h there was no S^{2-} in the system. This situation was certainly derived from the low S^{2-} concentrations in the clarified samples, because even after 4 h of the AO of unclarified samples S^{2-} could be detected.

The S^{2-} residual concentration after 4 h assay for the unclarified sample anodically oxidized by BDD, 4 mg L^{-1}, was less than that observed with PbO_2 and SnO_2, 13.5 and 12.9 mg L^{-1}, respectively. This also proves the efficacy of BDD in the S^{2-} removal.

The results for the SO_4^{2-} showed negligible decrease in its concentration during CC test, Tables 22 and 24. This shows that this treatment does not promote satisfactory reduction in SO_4^{2-} concentration. Regarding the samples submitted to EC, it was verified a slight increase in the SO_4^{2-} concentration, Tables 22 and 24. This situation may be due to the existence of oxidation phenomena that may occur during EC.

Regarding SO_4^{2-} concentrations after 8 h assay, it was observed substantial differences. While the final SO_4^{2-} concentrations of clarified samples by CC samples were approximately 1,300 mg L^{-1}, for those from EC, and non-clarified, the concentration of SO_4^{2-} was around 1,500 mg L^{-1}, Table 25. Such situation also shows the great effectiveness of CC in the S^{2-} removal, due to the low production of SO_4^{2-} observed at the end of 8 h of anodic oxidation, that is, it appears that the formed SO_4^{2-} during the anodic oxidation is predominantly formed from S^{2-} present in the system. This is ratified by the larger SO_4^{2-} concentrations observed in the samples subjected to EC and non-clarified, since in these cases the unsatisfactory removals of S^{2-} provided greater SO_4^{2-} formations during the anodic oxidation process. In the case of wastewater treatment process optimization, this seems to be very interesting, because the almost total S^{2-} removal by CC reduces competition for electrics charges, favoring the removal of carbonaceous and nitrogenous contaminants.

Further analysis of the results showed that the S^{2-}/SO_4^{2-} conversion presented peculiar characteristics. As can be seen in Table 26, the three electrodes formed greater quantity of SO_4^{2-} than that predicted, based on the available S^{2-} present in samples clarified by both CC and EC. A small advantage was observed for the SnO_2 electrode. This situation shows, once more, that SO_4^{2-} produced in the system is not only derived from S^{2-} oxidation, but also from the oxidation of intermediate sulfur species, in addition to the existing sulfur in organic compounds. In fact, the S^{2-} ion in solution can reacts forming several intermediate species between S^{2-} and SO_4^{2-}, such as in Eq. (47), (48), (56), (71) and (72), among others. Thus, the oxidation activities imposed by electrodes make not only the S^{2-} oxidation, but the oxidation of all present sulfur species.

The S^{2-} removal results for samples not clarified, showed that the BDD electrode was more efficient. The Table 27 shows that for the samples not clarified, SO_4^{2-} formation with BDD was lower, considering the S^{2-} removal by this electrode, i.e., the S^{2-} removed by this electrode is not necessarily converted to SO_4^{2-}. Moreover, although the SnO_2 electrode shows small S^{2-} removal efficiency, it provided large SO_4^{2-} production. Thus, can be inferred that while the BDD electrode is more efficient in S^{2-} oxidation and production of intermediate sulfur species, the SnO_2 electrode present high conversion ability of these species into SO_4^{2-}.

Table 26. Formed and expected SO_4^{2-} concentrations (mg L^{-1}) for all anodizing assays after 8 h.

SO_4^{2-}	CC			EC			without clarification		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
formed	97.6	82.4	70.0	96.2	92.6	84.7	216.1	212.6	151.0
expected	11.9	11.9	11.1	51.7	51.7	51.7	229.4	229.4	229.4

4.4.5.4 Chloride, Conductivity, pH and potential

The Cl^- concentration decreased during the experiments for all the different samples and applied processes, Figure 16a. This situation seems to be associated with Cl^- oxidation, namely to Cl_2, Eq. (32). It is important to highlight the lower final levels of Cl^- in the sample subjected to anodic oxidation by BDD, showing the superior Cl^- oxidation ability when compared to PbO_2 and SnO_2 electrodes.

BDD was the electrode that systematically presented the highest potentials, Figure 16b, probably due to the higher conductivity of the metal oxides electrodes (Fernandes et al., 2014).

For the non-clarified samples and those subjected to electro-oxidation by PbO_2 and SnO_2, post CC, a reduction in the potential during the anodic oxidation tests was observed, as can be seen in figure 16b. According to Costa et al. (2008), if the current densities are the same, the electrode potential reductions occur due to the increased conductivity of the sample. Thus, reduction of electrical resistance of the system appears to be derived from the increase of ionic species from molecules or ions present in the system, identifying the removal and/or conversion of contaminants.

The samples subjected to EC and anodically oxidized showed a slightly different behavior, since the potential practically did not change, Figure 16b, at same time that the conductivity, Figure 16c, showed negligible changes. This last event explains the relative constancy of the observed potential. This condition seems to be associated with the applied current density and high COD remaining due to the unsatisfactory contaminants removal by EC process, i.e., if the remaining organic load is high, and the applied electrical charge is low, oxidation processes will occur in the chemical structures more susceptible to oxidation or small species, without oxidation of larger chemical structure, with subsequent formation of smaller ionic chemical agglomerates, which would lead to a considerable increase in the conductivity and a decrease in the potential.

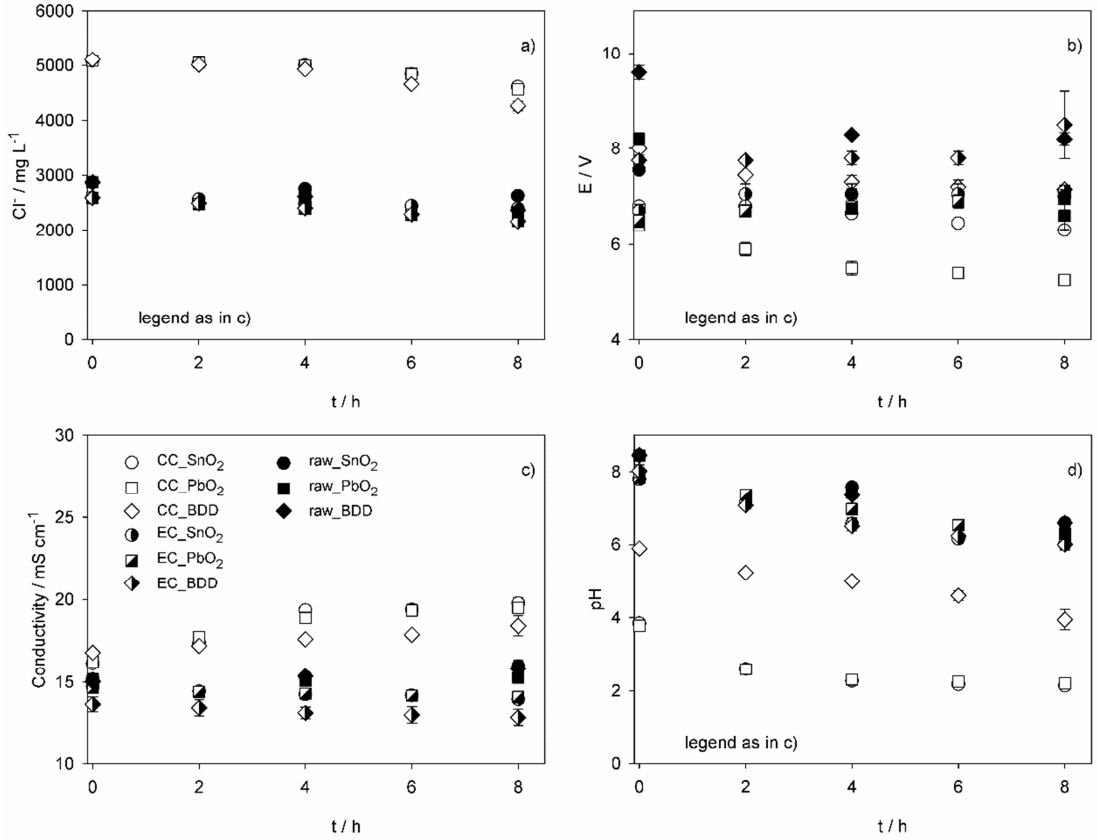

Figure 16. Dynamic of variations of: a) chloride concentration; b) potential; c) conductivity and d) pH, for all anodic oxidation assays. Duration 8 h.

The pH results demonstrated a reduction of this parameter on all the tests, as can be seen in Figure 16d. For BDD, this situation seems to be associated with the occurrence of the reaction represented by Eq. (41). As for the other two electrodes formed by metal oxides, Eq. (36) to (38) can explain the phenomenon. The strong odor of chlorine, Cl_2, observed in all three systems, showing its formation, associated with COD, DOC and TDC reductions, Eq. (32) to (34), also seem to be related to reduction of pH. The same analysis can be extrapolated to the reaction (35) related to the reduction of nitrogen load.

4.4.5.5 Specific Charge Consumption

Equation (80) was used to analyze the effect of the different electrode materials on the specific charge consumption.

For all anodically oxidized samples, it was noted that there was low energy consumption for BDD, Table 27. This situation is derived from its higher oxidation ability, compared to the other two electrodes, SnO_2 and PbO_2, and the reasons for this behavior were already discussed in section 4.3 of this thesis.

The results for samples clarified by CC proved to be very interesting, despite having similar charge consumption to those subjected to CE, the final COD levels are substantially lower, especially in the case to the PbO_2 and SnO_2 electrodes. A similar situation can be described for COD and TKN. The higher consumed electric charge for DOC removal, in relation to COD, in all cases, suggests the presence of complex organic molecules in the samples, which offer greater resistance to oxidation.

Whereas the applied electric charge to the EC in each sample was 1.4 kC and the contaminants removal rate was always lower than that observed for CC, the specific values of energy consumed for some parameters in the overall process, EC+AO, were higher than those recorded for CC+AO set, Table 27. Thus, it is noted that EC, as a preliminary treatment step for these effluents, is not as suitable as CC.

About the results of specific energy consumption observed for SO_4^{2-} formation, the values are aligned with the comments made in the S^{2-}/SO_4^{2-} conversion, with higher SO_4^{2-} production than expected.

Table 27. Specific charge consumption during AO assays: For COD, DOC and TKN - kC/g removed; for SO_4^{2-} - kC/g formed. Time duration: 8 h.

Parameter	CC			EC			without clarification		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
COD	26.6	29.8	12.6	30.7	35.6	10.8	8.7	8.2	7.0
DOC	120.5	148.8	54.4	112.5	129.5	46.0	53.2	44.5	29.7
TKN	115.1	118.4	44.4	158.1	157.2	74.5	65.2	60.8	59.8
SO_4^{2-}	221.3	262.0	308.4	224.4	233.3	255.1	100.0	101.6	143.0

In the time interval from 0 to 4 h, the SnO_2 and PbO_2 electrodes showed higher SC values for SA_CC samples, if compared to SB_CC with BDD electrode, Table 28. Although BDD electrode presents, in general, lower values than those obtained with metal oxide electrodes, in this case the low SC value observed for BDD seems to be from the higher COD content of the samples oxidized by BDD, Table 24, since only BDD was used for SB samples.

The lower energy consumption by BDD for COD removal can be checked in the SC values for samples submitted to EC, since in this case equal samples were used in the AO assays. Anyway, by comparing the results for 0 to 4 h and 4 to 8 h, in general, there was no great change in the SC for each electrode.

Table 28. Specific charge consumption during AO assays: For COD, DOC and TKN - kC/g removed; for SO_4^{2-} - kC/g formed. First 4 hours.

Parameter	CC			EC			without clarification		
	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD	SnO_2	PbO_2	BDD
COD	19.1	41.6	10.9	40.1	35.8	9.1	6.0	6.9	5.5
DOC	97.1	133.7	43.5	236.1	117.1	47.7	39.7	33.4	24.5
TKN	119.5	167.7	47.0	163.8	250.7	77.5	65.1	43.0	44.5
SO_4^{2-}	205.6	139.8	239.9	256.5	212.8	174.9	88.3	70.5	115.1

Most of the results obtained in this study regarding specific energy consumption are similar to those obtained in the previous study (section 4.3). However, the following general conclusions can be drawn: The energy consumptions for COD removals were always lower than those observed for the other parameters; the energy consumptions for DOC removals were always much higher than those observed for COD removal, i.e., COD is more easily removed than DOC. The comparison of SC for TKN removal for the first 4 h and the total time, 8 h, Tables 27 and 28, shows an increase in the energetic efficiency, since there was a decrease in the specific charge consumption for all clarified samples.

4.4.6 Conclusions

The results obtained have provided the following conclusions:

- The chemical coagulation has proven to be more efficient than the electrocoagulation to clarify the samples and reduce the levels of contaminants;

- The occurrence of biological activities significantly impact the quality of the effluent and acts as a harmful factor to further clarify the sample, either by chemical coagulation or by electrocoagulation;

- The chemical coagulation has proven to be a great ally as a preliminary treatment of tannery wastewater, since the anodic oxidation application is limited for this purpose;

- The energy consumption in the anodic oxidation processes by SnO_2 and PbO_2 are more strongly influenced by the concentrations of contaminants than those observed for the BDD;

- BDD anode proved to be very efficient in TKN removal, without, however, presenting similar efficiency in NO_3^- production. In this sense, the SnO_2 electrode presented the best ability to form NO_3^- from TKN;

- BDD electrode has the highest ability to make S^{2-} oxidation, although it presents great ability to produce intermediate sulfur species different from SO_4^{2-};

- SnO_2 anode, despite a low S^{2-} oxidation ability, is more efficient in converting intermediate sulfur species into SO_4^{2-}.

4.5 Chemical coagulation with iron ion, followed by two different experimental setups of anodic oxidation with recirculation

The aim of this work was to evaluate and compare the removal of organic load, nitrogenous compounds and sulfide from tannery effluents by chemical coagulation using iron cations, Fe^{3+}, followed by two different experimental set-ups of anodic oxidation:

- setup PS, where the clarified effluent is recirculated, passing first through an electrochemical reactor with a PbO_2 (P) anode and after that through an electrochemical reactor with a SnO_2 (S) anode, returning then to the first reactor (sample CC_PS);
- setup BDD, where the clarified effluent is recirculated through an electrochemical reactor with a BDD anode (sample CC_BDD).

The setups PS and BDD were also utilized with raw unclarified samples (raw_PS and raw_BDD, respectively), to compare the results.

The behavior of the Cr(VI) during the treatment process was also evaluated.

4.5.1 Experimental details

The effluent used in this work was sampled in the equalization tank of Curtumes Fabrício Lda, located in Vila Verde, Paranhos, Seia, Portugal. Usually, this company works with salted skins for the manufacture of leather. After the washing, the skins are submitted to dehairing with sodium sulfide, Na_2S. The effluent generated by washing and dehairing is sent for the equalization tank in which it is added hydrogen peroxide, H_2O_2, for a previous oxidation of the sulfide. The determination of the best dosage of clarifier, $FeCl_3$, was carried testing different concentrations of Fe^{3+}, 0.25, 0.5, 1.0 and 2.0 g L^{-1}, according to the methodology already described in subsection 4.3.1.

The recirculation system for the anodic oxidation assays, with 2,000 mL total volume, was composed by four vessels, R1, R2, R3 and R4, with 500, 200, 600 and 600 mL, respectively, working volumes. The recirculation was enabled by a peristaltic pump (P). The working volume for the pump and tubes was 100 mL. Electrodes were disposed in the recirculation system to give two different configurations, setup PS and setup BDD, Figures 17, a and b, respectively. Setup PS contained a PbO_2 anode in R3 and a SnO_2 anode at R4. Setup BDD contained only a BDD electrode at R3.

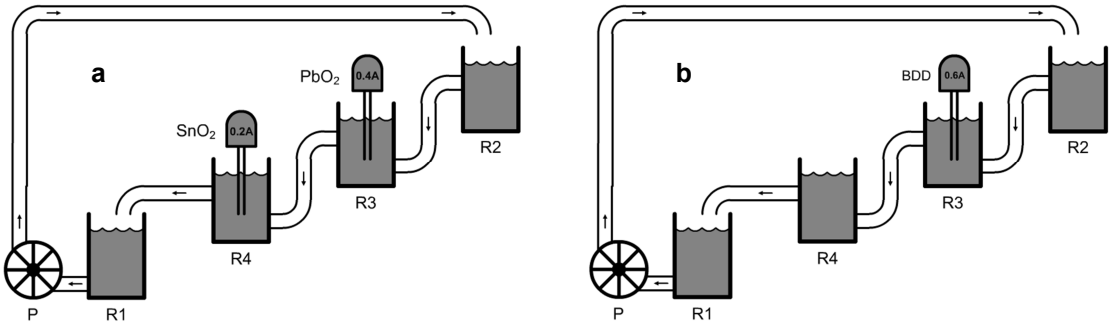

Figure 17. Recirculation system settings for the anodic oxidation assays: a) PS setup; b) BDD setup.

The experiments were conducted in batch mode with recirculation (3.6 L h^{-1}), for 8 h, using 2 L of clarified sample at room temperature (22-25 ^{o}C) without adding a supporting electrolyte. SnO_2, PbO_2 and DDB were used as anodes and a stainless steel plate was used as cathode. For all assays, the anode and the cathode were separated by 2 cm with 10 cm^2 of immersed area each one. The applied current intensity for setup BDD was 0.6 A; for SnO_2 and PbO_2, the current intensities were 0.2 and 0.4 A, respectively. Thus, the applied charge for each setup was 17,280 C. A power supply unit (Laboratory DC Power Supply, GPS-3030D model (0-30 V, 0-3 A) was used.

For each oxidation assay, 12 mL samples were taken in intervals of 2 h to determine the proposed parameters:, COD, DOC, TDC, DIC, TN, TKN, N-NH_3, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, S^{2-}, pH, conductivity, iron cation concentration, total chromium and Cr(VI) concentrations.

4.5.2 Wastewater characteristics

Table 29 shows the results of the characterization of the wastewater used in this study. The objective of the dehairing stage is to clean the skins and prepare it for the next step - the tanning. In addition of removing hair, in the dehairing process impurities adhered to the skin, such as fats, meat, etc, are also removed, i.e., a large volume of effluent with high organic load is produced at this stage. As can be seen in Table 29, the effluent presents considerable organic load, in addition to N-containing and S-containing species. The results for DOC and TDC showed that almost the totality (98%) of the carbon was in the form of organic carbon. This is in accordance with the characteristics of a fresh effluent from the dehairing step before any treatment, biological or chemical. Regarding nitrogenous species concentration, more than an half of the existing nitrogen is organic nitrogen, i.e., from the total nitrogen, 92% is TKN, being 38% N-NH_3 and 62% for organic nitrogen.

The presence of S^{2-} in the sample is due to sodium sulfide, used to remove hairs from the

skin. The high SO_4^{2-} concentration observed is due to the partial oxidation of the sulfide, because the company uses H_2O_2 to oxidize S^{2-} in the equalization tank.

During the leather processing, the skins are salty, to preserve them, which explains the high chloride concentration observed in the initial effluent. The high conductivity is due to the various substances associated with the process, such as Cl^-, S^{2-}, SO_4^{2-}, among others.

The high chromium concentration, 2,191.8 mg L^{-1}, was expected, since, according to Houshyar et al. (2012), from 20 to 40% of the added chromium in tanning process, usually in the form of $Cr(OH)SO_4$, remain in the final effluent. This explains also the high SO_4^{2-} concentration of the samples. This presents a problem to the tannery industry, because it prevents the direct biological treatment of the effluent. The reduced Cr(VI) concentration, 4.1 mg L^{-1}, was expected, since species such as S^{2-}, H_2S, $S_2O_3^{2-}$, etc, may reduce chromium, from (VI) to (III) (Guertin et al., 2005). Besides that, the stability of Cr(III) and the high oxidizing power of Cr(VI), Cr^{6+}/Cr^{3+} (E^o= 1.33 V), may also explain the Cr(VI) absence.

The presence of iron in the samples, 32.3 mg L^{-1}, may be associated with wear and tear of the devices used in the dehairing and tanning processes. It should be also considered the possible contamination of the chemicals used in process, water contamination, and the presence of iron in the skin, since iron is in the biological composition of the skins used in the leather industry.

Table 29. Physicochemical characteristics of effluent, with respective values of standard deviations. Conductivity in mS cm^{-1}; all other parameters, except pH, in mg L^{-1}.

Parameter	Average values (mg L^{-1})
pH	4.4 ± 0.1
Conductivity	58 ± 1
COD	5,463 ± 294
DOC	1,660 ± 106
TDC	1,685 ± 112
DIC	25 ± 7
$N\text{-}NH_3$	162 ± 5
TKN	400 ± 7
TN	422 ± 12
S^{2-}	58 ± 14
NO_3^-	34 ± 4
NO_2^-	< 5.0
SO_4^{2-}	9,209 ± 146
Fe	32 ± 3
Total Cr	2,192 ± 92
Cr(VI)	4.1 ± 0.5
Cl^-	10,671 ± 136

As already pointed out, the results differ substantially from those presented in the literature, since the characteristics of the samples are strongly influenced by the operating conditions of the leather production system at the moment of the sampling.

4.5.3 Clarification assays by Chemical Coagulation

The results from the effluent clarification tests are listed in Table 31. The clarification efficacy, i.e., lower final residual turbidity, was influenced by the concentration of the clarifying agent, being the maximum efficacy obtained for the iron concentration 0.25 g L^{-1}. The increase in turbidity for concentrations higher than 0.25 g L^{-1} was due to the excess of coagulant that reverses the neutralization of the superficial electric charge of the suspended particles and promotes negative impact in the clarification (Duan and Gregory, 2003). This was observed for iron concentrations of 0.50 and 1.00 g L^{-1}. The decrease in the residual turbidity for the iron concentration of 2.00 g L^{-1} was explained by Teixeira and Caliari (2005) (see also section 4.4.3 of this thesis).

Table 30. Residual turbidity with standard deviation after clarification by CC at the different hydrodynamics conditions.

Fe^{3+} (g L^{-1})	Turbidity (NTU)		
	Condition 1	Condition 2	Condition 3
0.00	1,120± 57	1,090 ± 14	1,080 ± 14
0.25	128 ± 11	168 ± 11	198 ± 11
0.50	302 ± 53	302 ± 4	422 ± 60
1.00	668 ± 187	512 ± 4	790 ± 57
2.00	125 ± 14	68 ± 4	98 ± 25

The results of the effluent characterization after CC are presented in Table 31. A decrease in the pH was observed probably due to the acid hydrolysis of the Fe^{3+} ion, described by the Eq. (7) to (9).

COD, DOC and TDC removals were 27, 8 and 14%, respectively. The COD removal was lower than those determined by Song et al. (2001), Ryu et al. (2007), Islam et al. (2011) and Chowdhury et al. (2013), that were 35.6, 64.8, 70 and 92%, respectively. According to Aboulhassan et al. (2006), the treatment with $FeCl_3$ proved to be effective in the pH range between 7 and 9, and the pH values for the referred works were between 7.5 and 12.9, 10.43 and 7.5, respectively. As can be seen in Table 29, the pH for this work was 4.4 and low COD removal was expected. Similar reasoning can be used to explain the TKN removal, since it was 10% in this work, whereas for Ryu et al. (2007) and Song et al. (2001) were 36.8 and 47.6%, respectively, for much higher pH values.

Regarding the N-NH_3, only 4% removal was observed, probably because the N-NH_3 is solubilized, which reduces its removal efficacy through coagulation/flocculation.

Table 31. Physicochemical characteristics of effluent after CC, with standard deviations and variation (%) due to CC. Conductivity in mS cm^{-1}; all other parameters, except pH, in mg L^{-1}.

Parameter	Average values	Variation (%)
pH	4.0 ± 0.0	-9
Conductivity	59 ± 1	0
COD	3986 ± 73	-27
DOC	1521 ± 32	-8
TDC	1540 ± 32	-14
DIC	19.7 ± 0.4	-37
$N\text{-}NH_3$	152 ± 4	-6
TKN	360 ± 10	-10
TN	389 ± 3	-8
S^{2-}	0.0 ± 0.0	-100
NO_3^-	42 ± 6	+24
NO_2^-	< 5.0	0
SO_4^{2-}	8692 ± 5	-6
Fe	268 ± 10	+762
Total Cr	2,060 ± 49	-6
Cr(VI)	1.1 ± 0.0	-73
Cl^-	10,900 ± 16	+2

4.5.4 Anodic Oxidation

4.5.4.1 Carbonaceous matter

The anodic oxidation of the clarified and raw samples after 8-h AO assay showed similar results in COD removal for both setups, Table 32 and Figure 18a. For samples pretreated with CC, removal rates were 20.3% (810 mg L^{-1}) and 21.7 % (865 mg L^{-1}) for PS and BDD setups, respectively. In the case of unclarified samples, at the end of the AO 8-h assay, the results presented yield with a slight advantage for the PS set. The removals rates were 34.8% (1,822 mg L^{-1}) and 31.5% (1,648 mg L^{-1}) for PS and BDD, respectively.

Although a better performance was observed in the removal rates for unclarified samples, if compared with the clarified samples, the final COD concentrations were always minor for unclarified samples, Table 32, i.e., the clarification by CC showed to be an interesting step for COD removal. Thus, the observed results in the COD removal for the CC+AO set were higher than those observed for the anodic oxidation of unclarified samples. This situation demonstrates once again the possibility of using AO as a polishing step in the treatment of tannery industry effluents, and the importance of the pretreatment as a factor for the best performance of the oxidation step.

Table 32. Final concentrations (mg L^{-1}), with standard deviations, of COD and DOC after 8 h of AO assay.

Electrode set	COD		DOC	
	After CC	Raw	After CC	Raw
PS	3,176 ± 44	3,408 ± 88	1,370 ± 6	1,318 ± 4
BDD	3,121 ± 24	3,581 ± 48	1,327 ± 5	1,372 ± 17

Regarding DOC removal, the results obtained for AO of clarified samples showed that the performance for BDD setup was slightly superior, almost the same removal rate, than that observed for PS set, Table 32/Figure 18b. The removals were 12.8% (195 mg L^{-1}) and 9.9% (151 mg L^{-1}) for BDD and PS, respectively. This shows the possibility of feasibility of using metal oxide electrodes in the replacing of BDD electrode in DOC removal.

For anodic oxidation of unclarified samples, the results showed no significant difference for PS and BDD sets, as can be viewed at Table 32. The DOC final concentrations in Table 32 and Figure 18b demonstrate that the clarification by CC made no difference in the final results, since the DOC final concentrations for clarified and not clarified samples were similar. This situation can be derived from the presence of organic compounds that present difficulty to be oxidized, limiting the action of the AO process.

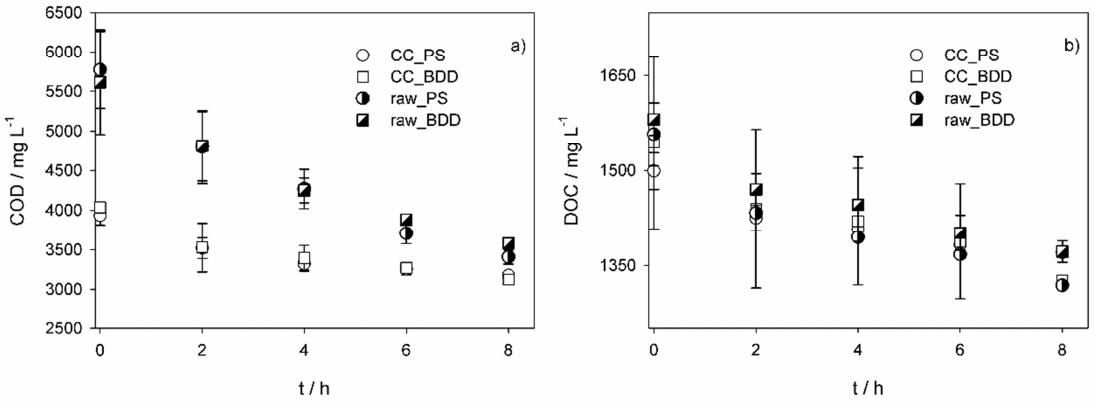

Figure 18. Changes in the concentrations of a) COD and b) DOC for the two tested sets for clarified and unclarified samples. Duration: 8 h.

Additional analysis showed that the DOC and TDC removals were virtually similar during the AO assays for clarified and not clarified samples. This demonstrates that the elimination of the carbon system, in particular in the form of CO_2, was limited to the oxidation of organic carbon present. In fact, over 98 % of the present carbon was organic carbon. However, despite its limitation, the data confirm that the AO can be exploited as a polishing step in the treatment of pretreated tannery effluent, e.g., by CC.

The high Cl^- concentration in the samples, Tables 29 and 31, the COD, TDC and DOC removals, and the strong characteristic odor of active chlorine, showed the participation of chlorine in the removal processes of organic matter, through indirect reactions, Eq. (32) to (34). However, according to Vlyssides and Israilides (1997), it is unable to completely oxidize the organic compounds. Thus, it can be inferred that the observed depletions in the COD, TC and TOC concentrations were almost exclusively derived from the reactions occurring on the surface of the electrodes.

4.5.4.2 Nitrogenous matter

The results showed similar efficiency for PS and BDD sets in the removal of ammonia nitrogen for all tested samples, Table 33/Figure 19c, with average yield of 26%. According to Szpyrkowicz et al. (2001), NH_4^+ in solutions containing Cl^- is indirectly oxidized according to equation (35), leading to nitrogen losses as N_2, Table 35/Figure 19c. The similar results can be associated with the high chloride concentration, Tables 31 and 33, that provides intense productions of HOCl (Eq. (32) and (33)), that, in turn, oxidizes the ammonia nitrogen to gaseous nitrogen (Eq. (35)), explaining the reductions in TN levels. The low pH for all samples, between 4.0 and 4.4, potentiates this situation, since at low pH the ammonia nitrogen tends to exist in the form of NH_4^+.

Table 33. Final concentrations (mg L^{-1}), with standard deviations, of TN, TKN, N-NH_3 and NO_3^- after 8 h of AO assay for clarified and raw samples.

Parameter	Pretreatment	Electrode Set	
		PS	BDD
TN	Raw	304 ± 5	315 ± 15
	CC	302 ± 6	315 ± 13
TKN	Raw	264 ± 31	252 ± 18
	CC	262 ± 13	252 ± 17
N-NH_3	Raw	124 ± 15	106 ± 3
	CC	113 ± 2	120 ± 6
NO_3^-	Raw	58 ± 1	102 ± 6
	CC	68 ± 6	98 ± 15

The reductions of ammonia nitrogen found by Rao et al. (2001) were higher, between 48.1 and 81.2%, for current densities ranging from 6.7 to 16.7 mA cm^{-2}. However, for these authors, the initial concentrations for ammonia nitrogen were between 102 and 105 mg L^{-1}, for chloride between 4,500 and 4,600 mg L^{-1} and for COD between 480 and 550 mg L^{-1}. Thus, the NH_4^+ removal observed in Rao et al. (2001) was intensified due to the low COD concentration, that wouldn't compete for the electric charges, the high chloride concentration and with the low NH_4^+ concentration.

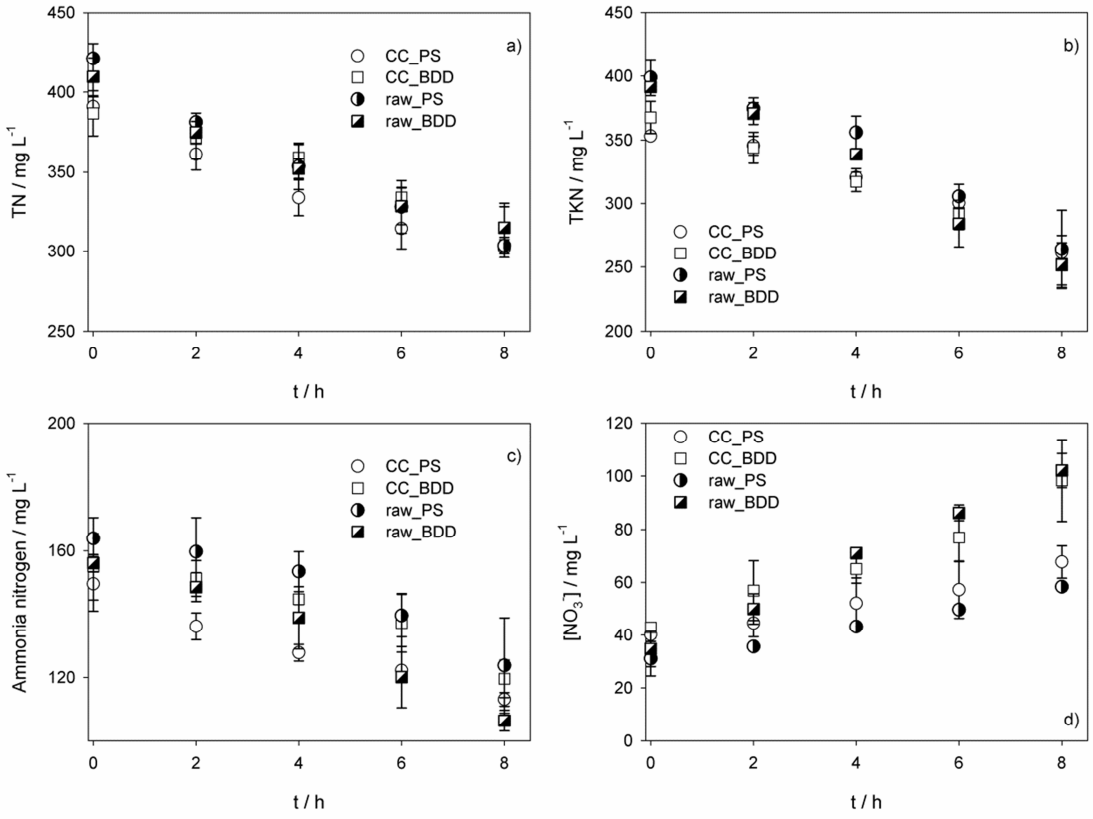

Figure 19. Changes in the concentrations of a) TN, b) TKN, c) ammonia nitrogen and d) nitrate for the two tested setups for clarified and unclarified samples. Duration: 8 h.

In face of the observed results, the application of AO after an anaerobic step seems feasible, since the anaerobic treatment promotes the conversion of organic nitrogen into ammonia nitrogen, in addition to the organic load removal, which could facilitate the nitrogen removal during the AO post-treatment. Moreover, the similar reductions of nitrogen load in the anodized samples by the PS and BDD sets show the feasibility of the application of PS electrodes in alternative to the BDD electrode for effluents treatment.

The NO_3^- formation, Table 33/Figure 19d, during the AO step, regardless of the type of oxidized sample, always presented the BDD set as the most efficient. The production of NO_3^- was 59% (average) higher in the BDD set when compared with the set PS, both for clarified samples for non-clarified. According to Brillas et al. (2007), the BDD electrode has greater O_2-overpotential than conventional electrodes and produces higher amount of reactive $^{\bullet}OH$, yielding an intense oxidation of the contaminants. In fact, the onset potential for O_2 evolution on BDD is higher than in PbO_2 and SnO_2 (Chen, 2004).

In all the assays, NO_2^- concentrations below 5 mg L^{-1} were found.

4.5.4.3 Sulfur compounds

The anodic oxidation results for clarified samples showed continuous production of SO_4^{2-}, Figure 20, which were higher for the BDD setup. The final concentrations were 8,819 mg L^{-1} (+1.4%) and 8,906 mg L^{-1} (+2.5%). This situation demonstrates that S^{2-} is not the only precursor of SO_4^{2-}, i.e., it seems that the S^{2-} initially present at samples is converted in several sulfur species that act as formers of SO_4^{2-} during the AO step. The S^{2-} removal will not prevent the increase in SO_4^{2-} concentration, unless all sulfur species are removed. Anyway, the presence of SO_4^{2-} in the final stage is better than other sulfur species, since intermediate sulfur species act as reducing agents, for example, reducing the dissolved oxygen levels.

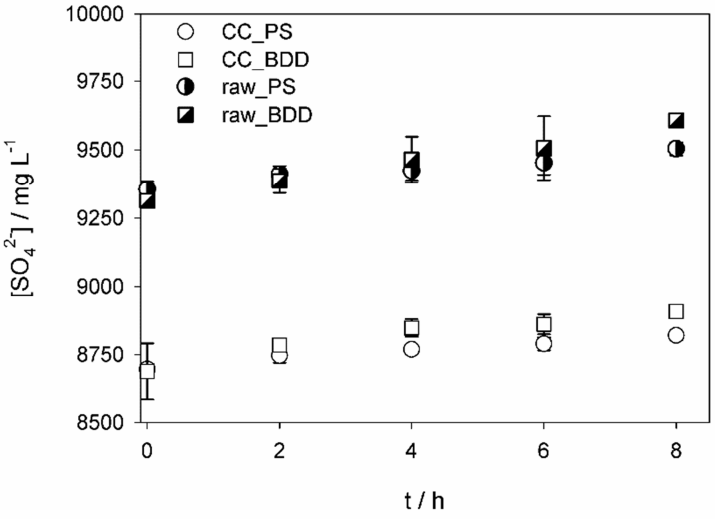

Figure 20. Changes in the concentrations of SO_4^{2-} during AO assays for all tested sets for clarified and unclarified. Duration: 8 h.

The SO_4^{2-} production in non-clarified samples was slightly higher than for clarified samples, Figure 20. It must be due to the presence of S^{2-} not removed by CC. This shows that the S^{2-} is also converted into SO_4^{2-} as the final sulfur species during the AO step. For non-clarified samples, the highest SO_4^{2-} production was observed for BDD setup.

The obtained results for sulfur removal, as for the other parameters, show the feasibility of using metal oxides electrodes, in special the PbO_2 and SnO_2 electrodes, for the oxidation of sulfur contaminants in wastewater.

4.5.4.4 Chromium

Whereas the total chromium concentrations remained virtually unchanged in all assays, the results for non-clarified samples showed a regular increase in Cr(VI) concentration during the assays with the PS setup that showed higher Cr (VI) production than at BDD setup, Figure 21. According to Souza et al. (1993), the oxidation of Cr^{3+} can be promoted by $^{\bullet}OH$ adsorbed at the electrode surface, Eq. (38) or (41), followed by equations (85) and (86).

$$Cr^{3+} + 3\ ^{\bullet}OH \rightarrow CrO_3 + 3\ H^+ \quad (85)$$

$$2\ CrO_3 + H_2O \rightarrow Cr_2O_7^{2-} + 2\ H^+ \quad (86)$$

The dynamics for Cr(VI) concentrations in clarified samples, Figure 21, show an increase in Cr(VI) concentration after 4 h assay, at PS setup, whereas for BDD setup, Cr(VI) formation was not observed. The electro-oxidation of Cr(III) may occurs in PbO_2 deposited over a Pb metallic surface, at potentials near the oxygen evolution potential [Pletcher and Tait (1981)]. In fact, Souza et al. (1993) observed the oxidation of Cr(III) to Cr(VI) on the surface of a lead anode coated with a PbO_2 layer. This can explain the high Cr(VI) production at PS setup.

On the other hand, according to several works (Schroeder and Lee, 1975; Saleh et al., 1989; Eary and Rai, 1991) Fe^{2+} ion can play an important role as reducing agent for Cr(VI) being the Cr(VI) reduction favored at acidic conditions (Kimbrough et al. (1999)). In fact, Eary and Rai (1991) observed the reduction of Cr(VI) by Fe^{2+} in solutions at pH between 2.5 and 5.5. The same behavior was detected by Sedlak and Chan (1997) in solutions with pH between 2.5 and 8.0. According to these last authors, Cr(VI) reduction can occur by reaction with Fe^{2+} through three one-electron-transfer steps (Eq. (87) to (89)). Meanwhile, the $Fe(OH)_3$ formed through Eq. (9) can react according to Eq. (90) [Green et al. (2006)]. Since the CC was performed with the addition of Fe^{3+}, Eq (90), followed by Eqs. (87) to (89), and Eqs. (85) and (86), can explain the absence (or low formation) of Cr(VI) in non-clarified samples at BDD set.

$$Fe^{2+} + Cr^{6+} \rightarrow Fe^{3+} + Cr^{5+} \quad (87)$$

$$Fe^{2+} + Cr^{5+} \rightarrow Fe^{3+} + Cr^{4+} \quad (88)$$

$$Fe^{2+} + Cr^{4+} \rightarrow Fe^{3+} + Cr^{3+} \quad (89)$$

$$Fe(OH)_3 + 2\ H^+ \rightarrow Fe^{2+} + ¼\ O_2 + 5/2\ H_2O \quad (90)$$

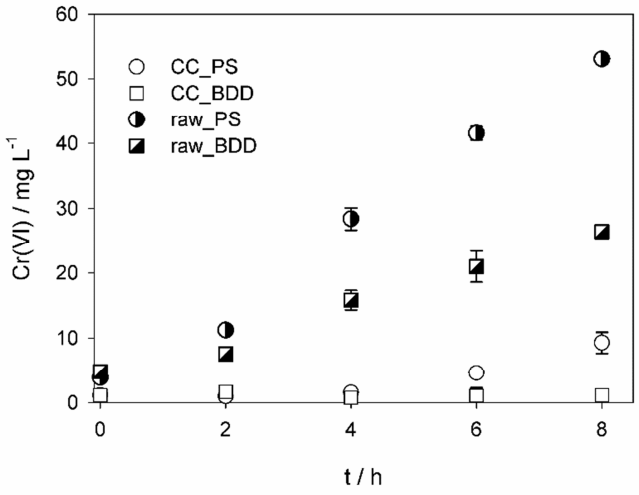

Figure 21. Variations for Cr(VI) concentration for all tested setups. Duration: 8 h.

4.5.4.5 Chloride, Conductivity, pH and Potential

The Cl^- concentrations decreased in all the assays, Figure 22a. This situation seems to be associated with the oxidation of Cl^- to Cl_2, and its elimination from solution, since a strong odor to Cl_2 was observed during assays.

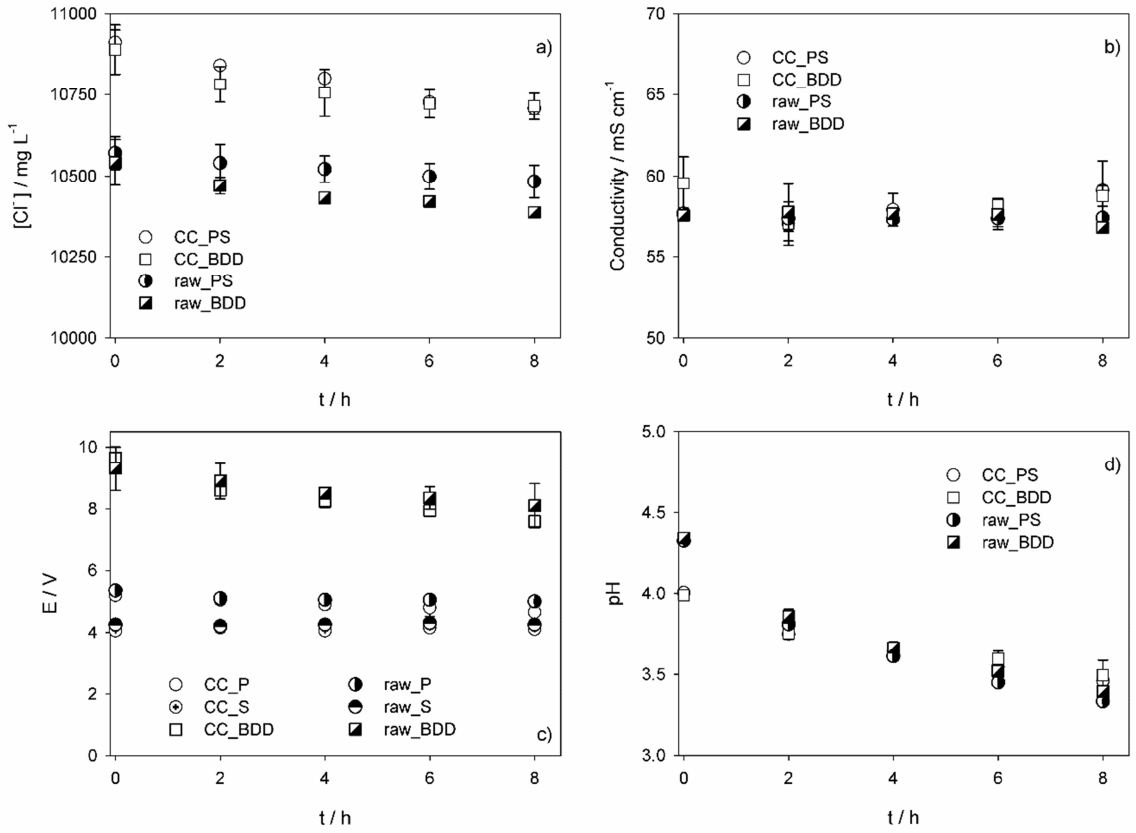

Figure 22. Variations in time of: a) chloride concentration; b) conductivity; c) potential and d) pH for all AO assays. Duration 8 h. In c) P stands for PbO_2 anode and S for SnO_2 anode.

The clarification influenced the variation of chloride concentration. As can be seen in Figure 22a, the chloride concentration decay was more pronounced in clarified samples. This behavior is associated to the lower organic load in the clarified samples, which reduces the competition for the electric charges, increasing the rate of the reaction described by Eq. 32. At BDD setup, the decrease in the chloride concentration during the assays is lesser influenced by the clarification process than at PS setup.

Table 34 shows the fitted equations for chloride concentration decay. The slope values for BDD setup, -20.53 and -17.93, for clarified and non-clarified samples, respectively, Table 34, also shows that the high BDD oxidant capacity was not greatly influenced by the clarification of samples, i.e., the oxidation capacity of chloride ion by BDD electrode is less susceptible to interference by contaminants, if compared with PS setup. On the other hand, the production of chlorine by PS setup shows that it is strongly influenced by the presence of contaminants, i.e., it is influenced for the competition by the electric charges, since the slopes were -10.87 and -26.21 for raw and clarified samples, respectively.

Table 34. Adjusted equations for chloride consumption during assays for clarified and raw samples. All tested sets. Duration time: 8 h.

Electrode Set	Equation	R^2 value	Sample
PS	-10.87 x + 10,567	0.987	Raw
	-26.21 x + 10,902	0.974	CC
BDD	-17.93 x + 10,523	0.921	Raw
	-20.53 x + 10,855	0.842	CC

The potential difference between anode and cathode for the clarified samples was slightly lower than that for non-clarified samples, Figure 22c. On the other hand, the conductivity for clarified samples were slightly higher than that observed for non-clarified samples, Figure 22b. Both results must be due to the $FeCl_3$ addition in the clarification step that increases conductivity and, consequently, decreases the potential difference.

The BDD set was the system that systematically presented the highest potential, Figure 22c. The lower potentials observed for the PS set, according to Fernandes et al. (2014) are due to the higher conductivity of the metal oxides electrode when compared to BDD.

During the assays, a slight reduction in the potential for PS setup was found, whereas for BDD setup, a clear reduction in the potential throughout the assays was verified. These facts must be related to the application of low current density in PS setup, 0.2 and 0.4 A for SnO_2 and PbO_2 electrodes, respectively, which is lower than that applied to BDD setup, 0.6 A. According to Costa et al. (2008), the reductions in the potential occur due to the increase in

conductivity, which is associated with the increase of ionic species from molecules or ions present in the system, identifying their removal and/or conversion into other species.

In all the tests, a reduction in the pH was observed, Figure 22d. This fact can be explained by Eq. (32). Eq. (36) to (41) also account for this observation (see also section 4.2.6).

4.5.4.6 Specific Charge Consumption

The Eq. (80) was used to analyze the effect of the different electrode materials on the specific charge consumption.

The results showed that the specific charge consumed for COD, DOC and TKN removals, and SO_4^{2-} formation, was lower for the samples non-clarified than for the clarified ones (Table 35). This must be due to the higher initial concentrations of contaminants in the raw samples. In general, BDD setup presented better energetic efficiency than PS setup.

Table 35. Specific Energy Consumption. For COD, DOC and TKN: C/g removed; for SO_4^{2-}: C/g formed. All AO assays. The first value is for 4 h assay; the second value is for total time.

Parameter	post CC		without clarification	
	PS	BDD	PS	BDD
COD	7.0 / 11.4	6.7 / 9.4	2.9 / 3.7	3.2 / 4.2
DOC	47.6 / 67.2	34.9 / 39.8	26.7 / 36.3	32.1 / 41.4
TKN	133.1 / 94.2	85.5 / 75.1	100.1 / 64.1	82.2 / 61.8
SO_4^{2-}	59.8 / 70.3	27.3 / 39.7	62.6 / 58.0	28.6 / 29.4

The charge consumption regarding COD, TKN and DOC removals were greatly increased by the introduction of a CC step in the assays performed with the PS setup, whereas with the BDD setup that increase in the charge consumption was not so pronounced, mainly in the DOC removal where a decrease was observed. It seems that CC removes the most easily oxidizable and mineralizable organic matter, leaving the most recalcitrant matter for the AO, even because the SC values regarding COD and DOC removal are always higher at 8 h than at 4 h.

Regarding charge consumption for TKN removal, it decreased with time for both setups. This behavior was already observed in other situations and can be explained if it is assumed that first is oxidized the most easily oxidizable carbonaceous matter, then the ammonia nitrogen, which reduces TKN, and only then the recalcitrant carbonaceous matter is oxidized.

For the AO assays run with the clarified samples, the specific charge consumption for the SO_4^{2-} formation increased with time, showing the effect of the diffusional step during AO, since most of the sulfur species had already been oxidized during CC. For the non-clarified assays, the SC slightly decreased with time for PS setup and slightly increased with time for BDD setup, but the differences may be considered within the experimental error.

The much lower values for charge consumption regarding TKN removal and SO_4^{2-} formation for the assays run with BDD setup may be due to a better performance of this system for species that are mainly oxidized by indirect processes, in the bulk of the solution. In fact, the chloride reduction is faster at the BDD setup than at PS setup, probably because BDD setup is more prone to form chlorine oxidizing species.

The TKN removal for clarified samples showed a better energetic efficiency in all assays for BDD setup. Furthermore, it was observed reduction of the specific charge consumption from the fourth hour of the assay. For clarified samples, the specific charge in the interval from 0 to 4 h was 133.1 and 85.5 C per (g of removed TKN), for PS and BDD setups, respectively. When considering the total time, 8 h, the specific charge consumption decreased in 29.2 and 12.3% for PS and BDD setups, respectively. This latter situation characterizes the difficult of removal the TKN, when compared with COD. In other words, the removal of contaminants started more intensely for COD, and the TKN was more intensely removed from the fourth hour of assay, after the reduction in COD concentration, as can be seen in Figure 18a and 19b.

The specific charge consumption for SO_4^{2-} formation was lower for non-clarified samples, for the two setups, Table 35. However, while the specific charge consumption for clarified samples remained approximately constant, if compared the time intervals 0 to 4 h and 4 to 8 h, for clarified sample, it was observed an increase of specific charge consumption, if compared the same time intervals. Thus, the scarcity of sulfur species increased the consumption of specific charge, that is, the system demonstrated diffusive control behavior. Anyway, the BDD setup showed greater energy efficiency, identifying it as the best system for SO_4^{2-} production from the conversion of several sulfur species.

4.5.5 Conclusions

The results obtained have provided the following conclusions:

- Although the chemical coagulation is effective for clarification of effluents, the pH of the solution is a very important parameter in the process and its control is necessary for a best performance;

- The energy consumption by the PS setup is more strongly influenced by the concentrations of contaminants than those observed for the BDD setup;

- Although the BDD presents great performance for contaminants removal by anodic oxidation, the PS setup proved the feasibility to replacement the BDD electrode, since the final results for contaminants concentrations were similar after the processes;

- The BDD setup presented a performance slight superior than PS set in SO_4^{2-} production from sulfur species, besides present the best specific charge consumption;

- The COD parameter showed great influence in the TKN removal, since the rate of TKN removal was dependent of COD concentration;

- Despite the anodic oxidation for treatment of effluents create conditions for Cr^{6+} formation, as from chrome in low oxidation states, the Fe^{3+} ion showed to act as an inhibitor of this process;

- Both systems tested showed similar behavior in removing TKN and ammonia nitrogen as N_2. However, BDD proved to be more efficient at converting nitrogen species into NO_3^-;

- The BDD setup showed best energetic performance for removing carbonaceous compounds than the PS setup.

5 CONCLUSIONS AND PROSPECTS FOR FUTURE WORKS

5.1 Conclusions

One of the main objectives of this thesis was to evaluate the performance of different electrode materials in the electrochemical removal of organic and inorganic loads from effluents collected in a Portuguese tannery industry. Three different materials were tested, namely, Ti/Pt/PbO_2, Ti/Pt/SnO_2-Sb_2O_4 and BDD, and the results obtained for several different effluents, collected in different seasons of the year and at different steps of the tanning process, have shown that electro-oxidation with the tested materials is undoubtedly a process that deserves attention to solve the environmental problems generated by this industry. In fact, for an effluent containing 30 g L^{-1} of COD with 8 h of anodic oxidation the COD removals were 42.4, 34.7 and 35.8% for BDD, Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4, respectively.

Since the organic load and suspended matter is very high in the tannery effluents, and electro-oxidation acts on the dissolved matter, studies on the application of chemical and electrochemical coagulations as pretreatment to the anodic oxidation were performed. These processes combination have shown to be also feasible treatments for tannery effluents. For an effluent with an initial COD of 5.3 g L^{-1}, COD removals varied between 56% (chemical coagulation, with aluminum salts, followed by anodic oxidation with BDD) and 63% (chemical coagulation, with aluminum salts, followed by anodic oxidation with Ti/Pt/SnO_2-Sb_2O_4).

When comparison is possible, chemical coagulation pretreatment proved to be more efficient in the COD removal than electrochemical coagulation. However, conditions were optimized for chemical coagulation and then reproduced for the electrochemical coagulation studies.

The behavior during the applied treatment processes of two specific pollutants from tannery industry, sulfide and chromium, was also assessed. During anodic oxidation, sulfide is converted to sulfate by a mechanism that involves a series of sulfur species, with different oxidation states, and that depends on the applied current density. Regarding the variation of Cr(VI) concentration during the performed treatments, it seems that chemical coagulation with iron salts preserves its formation from Cr^{3+} ions, either because Cr^{3+} ions are removed during chemical coagulation or because Cr(VI) is reduced to Cr^{3+} by Fe^{2+} ions.

The results obtained during the studies performed have provided also more specific conclusions:

- Oxidation of S^{2-} to SO_4^{2-} does not follow a single pathway, being dependent on the applied

current density; it occurs in stages characterized by the formation of sulfurous species, oxygenated or not, whose concentration decreases with the increase in applied current density.

- The formation of SO_4^{2-} is strongly influenced by the applied current density, due to the involvement of hydroxyl radicals and O_2electrogenerated by the water oxidation process.

- The clarification of the effluent showed to be an important step in the wastewater treatment;

- Clarification by iron cations proved to be more efficient than with aluminum cations, and chemical coagulation has proven to be more efficient than electrocoagulation to clarify the samples and reduce the level of contaminants. However, the pH of the effluent deeply influences the chemical coagulation process.

- In general, BDD electrode was more efficient in the contaminants removal, showing the highest energy efficiency. Moreover, the energy consumption by Ti/Pt/SnO_2-Sb_2O_4 and Ti/Pt/PbO_2 electrodes is more strongly influenced by the contaminants concentration;

- Ti/Pt/SnO_2-Sb_2O_4 electrode is not so efficient as BDD in the S^{2-} removal, being the initial removal rates of S^{2-} lower than the ones presented by BDD. However, Ti/Pt/SnO_2-Sb_2O_4 electrode is much more effective in the production of SO_4^{2-} from intermediate sulfur species. This is interesting because Ti/Pt/SnO_2-Sb_2O_4 is a less expensive material than BDD;

- Ti/Pt/SnO_2-Sb_2O_4 electrode presented small efficacy for the conversion of nitrogen forms into NO_3^-, and a good ability for their conversion into nitrogen gas. Thus, it is an interesting alternative for the removal of N-containing species from wastewater, avoiding eutrophication of the water bodies;

- The clarification with Fe^{3+}seems to act as an inhibitor in the conversion Cr(III) to Cr(VI), which is important because the anodic oxidation systems create conditions for the formation of Cr(VI) from Cr(III).

- Combining Ti/Pt/PbO_2 and Ti/Pt/SnO_2-Sb_2O_4 electrodes seems to be viable as an alternative to BDD electrode, since the results for the contaminant removals were similar for the two different experimental setups.

5.2 Future works

Although very important conclusions were obtained in this study, there are several aspects that must be considered to improve the performance of electrochemical processes to treat industrial tannery wastewaters. Some ideas of what can be done to pursue this objective are

presented bellow:

- Perform anodic oxidation assays at current densities higher than 30 mA cm^{-2} for clarified and unclarified samples, to study the influence of this parameter in the current efficiency and specific charge consumption.
- Evaluate the use of polyelectrolyte as auxiliary agents in the clarification step and its effects on the anodic oxidation step.
- Analyze the influence of the pH adjustment in the organic load removal rate from tannery effluents by chemical coagulation, with iron cations, and its influence in the anodic oxidation posterior step.
- Optimize the electrocoagulation process, namely studying the effect of initial pH, applied current intensity, duration of the assay, and settling process.
- Test other current densities combinations in the anodic oxidation with the PS and BDD setups.

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